TECHNOECONOMIC ANALYSIS OF A HYDROGEN PRODUCTION PROCESS USING PHOTOSYNTHETIC BACTERIA

Final Report

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INTRODUCTION

This report is a preliminary analysis of process design options for a hydrogen production process now being developed at the Solar Energy Research Institute (SERI) at Golden, Colorado. SRI performed this analysis for SERI under Subcontract No. BK-9-8281-02.

Hydrogen is a chemical raw material that is widely used for petroleum product upgrading (hydrotreating, hydrorefining, and hydrocracking) and for synthesis of products such as ammonia and methanol. Many methods of hydrogen production are in use today, although most hydrogen is produced from commercial hydrocarbon sources at refineries or ammonia plants. The older, less common processes for hydrogen production are coal gasification, the steam-iron reaction, and the electrolysis of water.

There is current interest in new sources of hydrogen for two main reasons. First, in the United States, the by-product hydrogen from petroleum refinery operation is almost fully utilized. Second, natural gas and naphtha, which in the past were readily available raw materials for hydrogen production for refinery use or for synthesis, are now very expensive and their long-term availability is in doubt.

The future requirements for hydrogen as a chemical feedstock or fuel and the poor economics of hydrogen transportation could lead to the development of small-scale localized hydrogen production facilities. It is possible that if low hydrogen demand areas are matched with suitable wastewater streams and sunlight availability, hydrogen might be supplied economically in low quantities by a biochemical process using photosynthetic bacteria.

OBJECTIVE AND APPROACH

The objective of this task effort was to prepare a preliminary review and analysis of the process being developed at SERI for the conversion of organic contaminants in wastewater streams to hydrogen using photosynthetic bacteria. SERI requested that a methodology be developed for assessing the process options. It was also requested that the following specific items be included in the final report:

- A review of alternative unit operations or processes
- Selection of specific unit operations or processes for analysis
- A summary of major process design assumptions and a preliminary design concept
- A block flowsheet with mass and energy balances
- A summary of major utility and operating requirements and costs (cost items shall be sufficiently detailed that SERI analysts can perform sensitivity analysis on major capital and production costs items)
- A calculation of process thermal efficiency
- Plant investment cost estimates (4th quarter 1980 dollars, factored level)
- Definition and sizing of major equipment items.

To analyze the process design options for the biochemical process, it was necessary to first select an appropriate scale of operation. The scale of operation was determined by considering current hydrogen production and demand levels, process stoichiometry, quantities and concentration of contaminants available in wastewater streams, and land requirements. Once a specific scale of operation was selected, alternative unit operations or processes were considered. A process flow sheet was prepared and investment and operating costs were estimated.

BACKGROUND ON HYDROGEN PRODUCTION AND PROCESS ECONOMICS

Hydrogen is now an important chemical raw material and is being considered as a potential fuel. Hydrogen is attractive as a fuel because it can be produced from water and because its combustion creates little or no atmospheric pollution. On a weight basis, hydrogen has two or three times the combustion energy of petroleum hydrocarbons. It can be transmitted and stored in a manner similar to that of natural gas, and the technology of its production is well developed. However, high production costs and the complexities of cryogenic or pressurized handling and transport may reduce the large-scale use of hydrogen as a fuel.

Two types of merchant hydrogen are available--compressed gas (in cylinders, tanks, or pipelines) and liquid. Liquid hydrogen is shipped by tank car, truck, or barge. Current prices for liquid hydrogen range from $9.50 to $10.80 per 1000 SCF in 13,000-gal. lots (Chem. Week, 1981). Pipeline hydrogen prices are near $3.00 per 1,000 SCF for the largest captive users (C&E News, April 1980).

Total hydrogen requirements are expected to increase three-fold by the year 2,000 (Corneil, 1980) and steam reforming of natural gas is expected to be the preferred method of large-scale hydrogen production; however, other methods may prove to be economical in certain regions for small-scale production.

In the remainder of this background section, data from several literature sources on investment costs and total product costs for different hydrogen production options are discussed to provide a perspective on hydrogen production costs by nonbiochemical processes. We have not attempted to revise these cost estimates so as to put them all on the same cost basis (i.e., equivalent plant capacities). Therefore, comparisons of costs between sources should not be made.

The production of hydrogen in the United States is estimated to be greater than 2 billion SCFD, 30% of which is captively consumed in petroleum refinery operations. The largest outlet is still ammonia manufacture, which represents about 59% of the U.S. hydrogen requirements. The remaining 11% is used for methanol production and by small consumers. Merchant hydrogen production represents a small portion of total capacity (< 10%) and is estimated to be about 48 billion SCF in 1980 or 130 million SCFD (C&E News, 1980). The commercialization of processes for synthetic fuels or synthetic natural gas together with increased refinery capacity are projected to increase refinery hydrogen requirements sixfold by the year 2000 (Corneil, 1980). Future hydrogen requirements for ammonia production also will double in the next 20 years.

Steam reforming, residuum partial oxidation, and Koppers-Totzek (K-T) coal gasification are processes now used to produce hydrogen in the range of 50 to 100 SCFD. Other coal gasification processes are being developed such as the high-pressure partial oxidation process (Texaco, Shell and Koppers-Totzek) (Corneil, 1977; Kelly, 1976; Gregory, 1975). Table 1 shows some technical considerations for existing hydrogen production technology. The cost of manufacturing hydrogen, for several processes shown in Table 2, has been calculated by Corneil and Heinzelmann at Exxon in 1976 (Corneil, 1980).

At the 100 million SCFD level, the most attractive method of producing refinery hydrogen is steam reforming of natural gas due in part to the lower investment cost.

Estimated hydrogen production costs are shown in Table 3 for 880 SCFD plants prepared by the National Research Council (Berry, 1980). A major cost disadvantage is seen for electrolysis systems for such large production facilities.

The Futures Group Inc., in a study for EPRI, showed that for a 0.1 MM SCFD plant or smaller the capital cost is lower for an electrolyzer than for steam reforming. Estimates for a 0.1 MM SCFD plant give the total cost of hydrogen from an electrolyzer (SPE) as $5.51/1000 SCF and for steam reforming as $8.54/1000 SCF. These results would support the use of electrolysis to make merchant hydrogen or for specific uses in small volume applications (Berry, 1980).

TABLE 1

TECHNICAL CONSIDERATIONS IN THE SELECTION OF HYDROGEN PRODUCTION PROCESSES

			Hydrogen Product			
Hydrogen Process	Alternative Feedstocks	Additional Major Raw Materials	Purity (%)	Press. (psig)	Salable By-Products	Technical Status
Steam reforming of natural gas	Light hydrocarbons	None	96 to 98	250 to 400	None[*]	Well-developed
Steam reforming of naphtha	Low viscosity volatile hydrocarbon liquids	None	96 to 98	250 to 400	None[*]	Well-developed
Noncatalytic partial oxidation of residual oils	Wide range of light to heavy hydrocarbons plus coal and coke	Oxygen	≅97	1500 to 1800	Sulfur	Well-developed
Catalytic partial oxidation of naphtha	Volatile hydrocarbons	Oxygen	≅98	Up to 300	None[*]	Well-developed
Catalytic decomposition of methane	Light hydrocarbons	None	93 to 94	200 to 300	Possibly low-Btu fuel gas	Limited development
Gasification of coal	Coke and other carbonaceous solids	Oxygen	≅97	Up to 450	Sulfur	Well-developed or still being developed
Steam-iron reduction of water	Coal, coke, carbonaceous solids, or hydrocarbon sources of CO gases	Steam	98 to 99	Up to 15	Possibly sulfur; also steam and fuel gas[†]	Technology old; limited new development
Electrolysis of water	None	Electricity	99.99	Up to 300	Oxygen	Well-developed

---

[*] Natural gas and naphtha feed materials are assumed to have been previously desulfurized.

[†] Process could be designed for internal use of this by-product steam and fuel.

According to DOE estimates, the minimum size for a SPE plant that would supply commercial users is 50,000 SCFD (Mezzina, 1980). The large production volumes discussed earlier would exist only in certain regions and industries.

Table 2

HYDROGEN COST COMPARISON IN 1980 DOLLARS FOR A 100 MM SCFD PLANT

	Natural Gas Steam Reforming	Residuum Partial Oxidation	Coal Gasification K-T	Coal Gasification New
Investment cost (MM$)	63	159	246	200
Manufacturing cost* $/1000 SCF	1.68	2.55	2.70	2.25

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*Assuming 275 Btu/SCF H_2.

Table 3

COMPARISON OF HYDROGEN PRODUCTION COST FOR A 880 MM SCFD PLANT

	Steam Reforming	Coal Gasification	Electrolysis
Overall thermal efficiency (%)	70	60-65	32 SPE† 21-25 KOH
Estimated hydrogen production costs (1980 $/1000 SCF)	1.87	2.61	5.40

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†SPE = Solid Polymer Electrolyte, General Electric.

SOLAR ENERGY UTILIZATION FOR HYDROGEN PRODUCTION

One problem with using solar energy for hydrogen production is the cost of collection. The surface of the earth receives about 1000 watts/m^2 (2000 Btu/ ft^2/day) of radiation, which can be directly collected at about 250°F. Concentration of solar radiation to give higher temperatures (i.e., thermal power plant operating temperature) requires substantially higher costs. Another disadvantage of solar energy is its diurnal nature; that is, the capital tied up in solar collectors or reactors is used only 50% of the time or less. The successful use of solar energy to produce hydrogen must center on low cost or highly efficient collection of energy. Biological collection and conversion could prove to be more economical than other solar-electric or photochemical approaches.

Direct Use of Solar Radiation

Solar radiation at wavelengths below 552 nm contains sufficient energy to decompose water directly. However, water does not absorb light appreciably at wavelengths above 185 nm and light at wavelengths below about 300 nm is absorbed by ozone in the upper atmosphere. An energy transfer mechanism is required to allow the photon energy (between 300 and 552 nm) to decompose water directly.

Several methods of energy transfer have been proposed. Photovoltaic cells can generate the voltage needed to split water electrolytically. Heterogeneous photo-assisted redox reactions generally refer to reactions at semiconductor surfaces such as n-type TiO_2 and platinum electrodes. Homogeneous photo-assisted redox reactions refer to direct irradiation of solutions that contain organic dyes or inorganics capable of absorbing solar radiation and transferring it to water for photolysis.

Photosynthetic Production of Hydrogen

Photosynthetic bacteria can use organic acids, carbohydrates, and alcohols in the presence of light as the hydrogen donors for H_2 production as follows:

$$(CH_2O) + H_2O \xrightarrow[\text{bacteria}]{\text{light}} CO_2 + 2H_2 \qquad (1)$$

The reactions must take place under anaerobic conditions because oxygen inhibits the nitrogenase enzyme system.

The possible substrates for photosynthetic bacteria are listed in Table 4.

Feedstocks for a photosynthetic hydrogen production facility could include municipal wastewater or industrial wastewaters from food processing operations, the pulp and paper industry, the chemical industry, or the textile industry. Food processing wastestreams in many cases contain large concentrations of carbohydrates and sugars, fats and oils, and proteins and amino acids. The costs for treating such wastewater streams are generally quite high. Thus, an economical advantage is gained if a high value product such as hydrogen or methane can be produced during the waste treatment process. The bacterial mass formed in the process may be collected and used as a protein source or as a fertilizer and soil conditioner.

Highest hydrogen productivities have been found with organic acids such as lactic acid. Table 5 shows the hydrogen-producing activity of several organisms studied by Weaver at SERI (1980). The most promising organisms to date belong to the genus Rhodopseudomonas producing 6.7 g moles of hydrogen/liter of culture/hr at ~ 1 g dry wt. cells/liter. The maximum activities presented in Table 5 were found using lactate as a substrate and may not hold for other organic acids or sugars. The development of other wild types or genetically engineered strains may lead to wider substrate use and higher activities. Alternatively, mixed cultures could be used for hydrogen production from complex substrate feedstreams. Other mutants could be improved by increasing the efficiency of photosynthesis or increasing nitrogenase activity.

The activities presented in Table 5 are for controlled-batch systems. It may be unrealistic to assume that the same rate will apply for an outdoor culture system that could have temperature and pH fluctuations, multiple substrates, light limitation, poor mixing zones, and inhibiting components in the media. One such inhibiting component is organic nitrogen

Table 4

SUBSTRATES UTILIZED BY PHOTOSYNTHETIC BACTERIA

Sugars

- Cellobiose
- Sucrose
- Glucose
- Fructose
- Mannose
- Galactose
- Ribose
- Xylose

Sugar Alcohols

- Mannitol
- Sorbitol

Sugar Acids

- Gluconic acid
- Glucuronic acid

Organic Alcohols

- Ethanol
- Glycerol
- Propanol
- Butanol
- Isopropanol

Inorganic Donors

- Sodium thiosulfate
- Hydrogen sulfide

Organic Gases

- Methane
- Carbon monoxide

Organic Acids

- Acetic acid
- Lactic acid
- Pyruvic acid
- Formic acid
- Succinic acid
- Propionic acid
- Butyric acid
- Isobutyric acid
- Citric acid
- Fumaric acid
- Malic acid
- Tartaric acid
- Valeric acid
- Caproic acid
- Caprylic acid
- Pelargonic acid
- Malonic acid
- Glycolic acid

Aromatic Acids

- Benzoic acid

Natural Substrates

- Alcohol stillage
- Fermented corn
- Fermented milk
- Fermented orange juice
- Fermented grapefruit
- Fermented peach

Table 5

REPRESENTATIVE RATES OF H_2 PHOTOPRODUCTION FROM PHOTOSYNTHETIC BACTERIA*

Organism	Activity $\frac{\mu l\ H_2}{mg\ dry\ wt\ hr}$	Comments
Rhodopseudomonas capsulate SCJ	168	Lactate as C-source
Rhodopseudomonas capsulate B10	124	Lactate as C-source
Rhodopseudomonas sulfidophila BSW8	106	Lactate as C-source
Rhodopseudomonas viridis NTHC 133	3	Lactate as C-source
Rhodospirillum rubrum S-1	146	Lactate as C-source
Rhodopseudomonas palustris EC	62	Lactate as C-source
Rhodopseudomonas palustris EC	2	Celluose as C-source
Rhodopseudomonas sulfidophilia BSW8 plus an unidentified marine species	6	Agar as C-source
Rhodopseudomonas capsulate W12 (B10 Nif^-)	3	Lactate as C-source
Rhodopseudomonas capsulate W52 (B10 Hup^-)	144	Lactate as C-source

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*From Weaver 1980.

(ammonia, nitrites, nitrates). The hydrogen-producing organisms will grow on the carbon substrates until the nitrogen sources are consumed. If light is provided, doubling times may approach 1.75 hr with ammonia serving as the nitrogen source (Weaver, 1980a). Higher doubling times ($>$ 10-fold increase) are found when nitrates and/or nitrites serve as the nitrogen source. If the organic nitrogen concentration in a feedstock stream is high, many hours of daylight may be required for growth before hydrogen production will begin. A high initial biomass concentration will speed nitrogen consumption, but high nitrogen concentrations may lead to significant substrate losses and excessive biomass production. The feed-stream may have to be denitrified before it can be used for hydrogen production.

The hydrogen produced does not undergo any chemical reaction and, being slightly soluble, is transported quantitatively into the gas phase.

Portions of the carbon dioxide produced will remain dissolved in the media, react chemically to form bicarbonate or carbonate, be transported to the gas phase, or precipitate as carbonate ($CaCO_3$). The extent to which these reactions occur will be influenced by the wastewater characteristics (alkalinity, pH) and the gas flow rate and gas composition. We have assumed, however, that essentially all of the CO_2 will enter the gas phase and that the product gas will contain 66% H_2 and 33% CO_2 on a dry weight basis. This gas would be processed to give a high purity hydrogen product that could be stored for captive use, transported by pipeline, or liquified and shipped by rail.

CALCULATION PROCEDURES

All calculations presented in this report are based on an average value of 150 x 10^{-6} liters H_2 (STP)/hr/10^{-3} g dry wt. cells*, which is equivalent to one of the maximum hydrogen production rates reported by Weaver (1980) of SERI (see Table 5). This value is used in Table 6 to describe the relationship between cell mass concentration (C_c), initial substrate concentration (C_s^o), and reactor volume (V_R).

To illustrate how land requirements will vary depending on the substrate concentration and the reactor depth, we have assumed that shallow flow channel reactors will be used. These reactors are designed to take advantage of the intermittent light effect (see Appendix A.) Concentrated wastestreams (> 1 g/l CH_2O equivalent) are the most attractive because the reactor volume is directly proportional to the substrate concentration. To produce 1 million SCF/day of hydrogen with a substrate utilization factor of 0.8 and a cell mass concentration of 1 g/liter requires a reactor volume of 23.6 million liters.† The tonnage of substrate required is 23.6 metric tons/day.

only Requires 6 x 10 [illegible]

Figure 1 shows the reactor surface area versus hydrogen production for several substrate concentrations and reactor channel depths. The land requirements to produce 1 million SCF of hydrogen per day could range from 6 to 1200 acres (a factor of 200) over the range of substrate concentrations and channel flow depths considered (5 to 10 cm).

4 × 2000 [illegible]

1200 [illegible]

Solar input

1 × 10 ft³ [illegible]

3 × 10 BTU

50%

This is just plain wrong

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[*] This is equivalent to ~ 1 volume of H_2 gas/5 volumes of cell suspension/hr.

[†] Assuming 8 hr/day of reactor operation.

Table 6

SAMPLE CALCULATION OF REACTOR VOLUME

Basis: $\frac{150 \times 10^{-6}\ LH_2\ \text{(at STP)},}{hr\ \ 10^{-3}\ g\ cells}$ 1×10^{6} SCF H_2/day or 28.3×10^{6} LH_2/day, 8 hr or reactor operation/day

Substrate concentration never limiting, substrate utilization factor of 0.8

Calculations

$$\frac{28.3 \times 10^{6}\ LH_2}{day} = \left(\frac{150 \times 10^{-6}\ LH_2}{hr\ 10^{-3}\ g\ cells}\right)\left(C_c\ \frac{g\ cells}{L}\right)\left[\left(V_R\ L\right)\left(\frac{t\ hr}{batch}\right)\left(Y\ \frac{batches}{day}\right)\right]^{*}$$

$$\left(C_c\right)\left(V_R\right)\left(t\right)\left(Y\right) = 1.9 \times 10^{8}\ g\ cells \cdot hr/day$$

where $tY \equiv 8$ hr/day

$$\therefore\ C_c\ V_R = 23.6 \times 10^{6}\ g\ cells$$

$$V_R = 23.6 \times 10^{6}\ g\ cells/C_c$$

V_R is assumed equal to the volume of waste required each day, C_c is constant.

The volume of waste required is determined by the initial substrate concentration C_S^o in g/L and the substrate utilization factor f, which is defined as the ratio of substrate consumed for H_2 production to the total amount of substrate initially available.

$$\frac{\dfrac{28.3 \times 10^{6}\ LH_2}{day}\ \ \dfrac{0.67\ g\ \ CH_2O^{\dagger}}{LH_2}}{0.8} = \frac{23.6 \times 10^{6}\ g\ CH_2O}{day}$$

Total substrate requirement per 10^{6} SCF H_2/day

Table 6 (Concluded)

$$V_R = 23.6 \times 10^6 \text{ g } CH_2O/C_s^o$$

Substitute for V_R

$$\frac{23.6 \times 10^6 \text{ g } CH_2O}{C_s^o \text{ g } CH_2O/L} = \frac{23.6 \times 10^6 \text{ g cells}}{C_c \text{ g cells}/L}$$

$$\therefore \quad C_c^o \cong C_s^o$$

$$\text{For } C_s^o = 1 \text{ g}/L = C_c$$

$$V_R = 23.6 \times 10^6 \text{ L}$$

$$\text{Tonnage of substrate} = \frac{23.6 \times 10^6}{\text{day}} \times \frac{1 \text{ g}}{\text{L}} = \frac{23.6 \times 10^6 \text{ g}}{\text{day}} \text{ or } \frac{23.6 \text{ metric tons}}{\text{day}}$$

---

[*] 8 hours of operation day, t = 8 hr.

[†] $\frac{1 \text{ g mole } H_2}{22.4 \text{ L } H_2} \quad \frac{1 \text{ g mole } CH_2O}{2 \text{ g mole } H_2} \quad \frac{30 \text{ g } CH_2O}{\text{g mole } CH_2O} = \frac{0.67 \text{ g } CH_2O}{\text{L } H_2}$

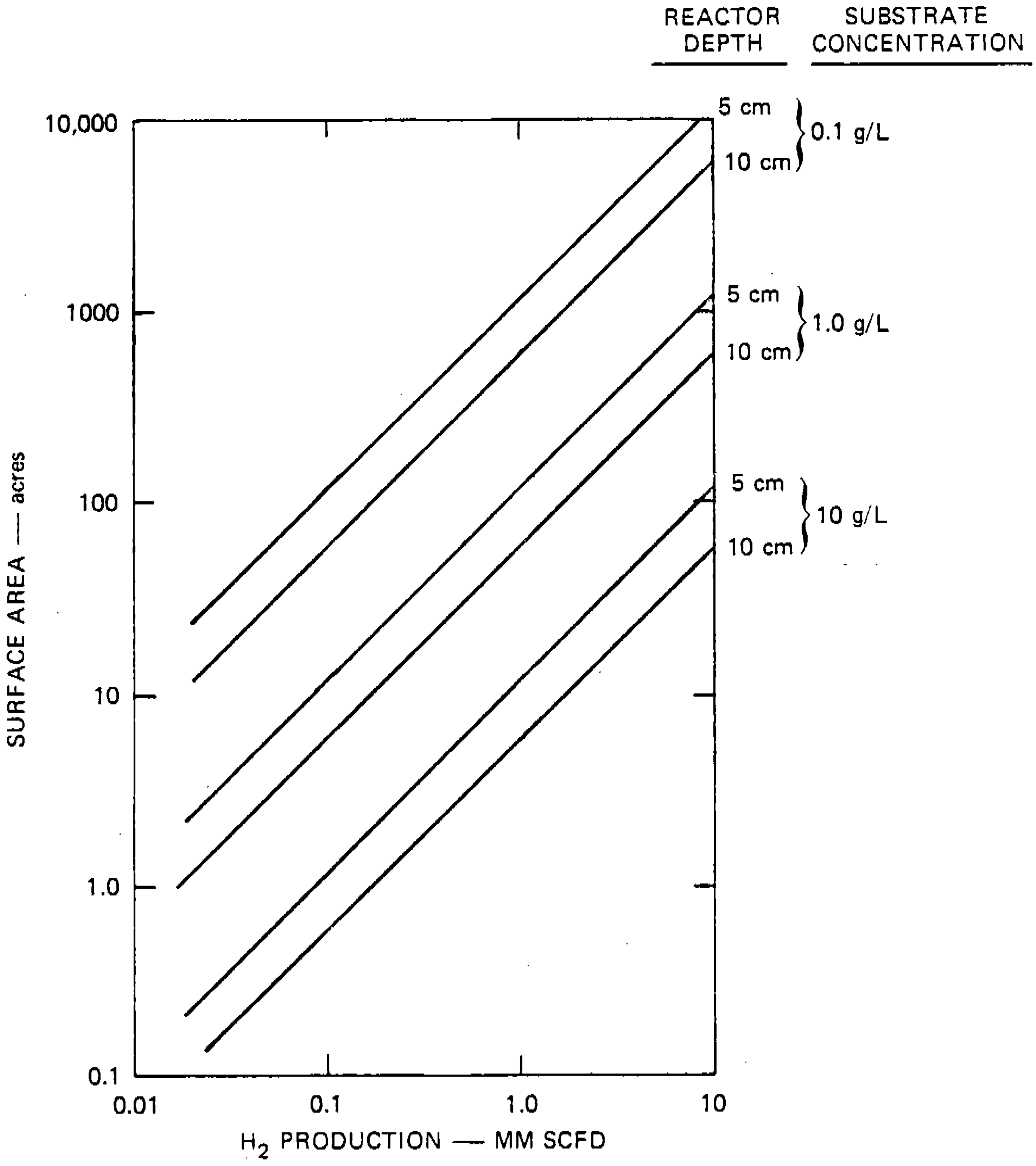

FIGURE 1 REACTOR SURFACE AREA REQUIREMENTS VERSUS HYDROGEN PRODUCTION
At 0.1, 1, and 10 g/L substrate concentration and reactor depth of 5 or 10 cm.

SYSTEM DESIGN CONSIDERATIONS AND OPTIONS

Basis for the Technical Analysis

Table 7 presents information on waste volumes and substrate sources for photobiological hydrogen production. Hydrogen production levels from wastewater streams will probably never exceed 10 million SCF/day at any site. It appears reasonable to assume that most H_2 production facilities will fall within the capacity range of 0.1 to 10 million SCF/day. A base case facility for consideration will be assumed to have a capacity to produce approximately 1 million SCF of H_2/day. Because $C_c = C_s^o$ (see Table 6), it will probably be necessary to keep C_s^o below 5 g/liter because a high cell mass concentration will be difficult to maintain. Therefore, dilution of the more concentrated wastes may be necessary. We assume that the base case facility has a substrate concentration of 2.5 g/liter.* To produce 1 million SCF of H_2 per day (28.3 million liters) will require 23.6 metric tons/day of CH_2O substrate. Therefore, the volume of waste required at a substrate concentration of 2.5 g/liter will be 9.4 million liters/day or 2.5 million gallons/day. The flow channel depth will be assumed to be 5 cm (2 in.). The reactor surface area is estimated to be equal to 19 hectares, or 47 acres.

Process Areas and Unit Processes

Table 8 lists process steps that might be required in a photobiological hydrogen production facility. The particular steps required would depend on the specific physical, chemical, and microbiological characteristics of the wastewater; the availability of support services (shops, labs, offices) and utilities from the waste generating source or facility; the physical characteristics of the site; and the specific markets or uses for the hydrogen and by-products.

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*This level of cell mass concentration has not been achieved with the hydrogen-producing organisms studied at SERI; 1 g dry wt cells may be an upper limit.

Table 7

POTENTIAL FEEDSTOCKS AND ESTIMATED PRODUCTION VOLUMES FOR PHOTOBIOLOGICAL HYDROGEN PRODUCTION

Wastestream	Substrate Conc. (g/L)	Volume (L/day)	Substrate Tonnages (Metric tons/day)	H_2 Prod. (MM SCFD)
Untreated municipal wastewater*	0.1-0.2	$10^6 - 10^9$	1.0-200	0.04-9
Paper and pulp, sulfite liquor	15-20	$10^5 - 10^7$	1.5-250	0.06-11
Food processing, acid whey	50	$10^4 - 10^6$	0.5-50	0.02-2
EtOH fermentation stillage	1-5	$10^5 - 10^7$	0.1-50	0.01-2
Anaerobic digester supernatant	0.2-0.3	$10^4 - 10^7$	0.002-3	0.0-0.1

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*There are ~ 21,000 publicly owned wastewater treatment works (POTW) in the U.S. From 95% to 98% of these POTWs have average design flow capacities of ≤ 4 x 10^7 liters/day. These plants treat about one-third of all wastewater. About 40% of all municipal wastewater is treated by about 200 large POTWs with capacities of more than 1 x 10^8 liters/day.

Table 8

PROCESS STEPS FOR CONSIDERATION IN A PHOTOBIOLOGICAL HYDROGEN PRODUCTION FACILITY DESIGN

	Options	Comments
Wastewater Storage and Pretreatment		
• Sterilization or Pasteurization	Heating by steam injection or use of a recuperative type heat exchange system; UV-light	Could use solar collectors for preheat. Chemical agents are probably not acceptable.
• Concentration	Membrane processes such as ultrafiltration; multiple effect evaporators perhaps with thermal recompression or vapor recompression; freeze concentration.	Concentration processes could sterilize.
• Dilution	Effluent recycle; other process wastewaters; fresh water.	
• Solids Removal	Gravity sedimentation--perhaps during storage; centrifugation; filtration	--
• Nitrification/Denitrification	Two stage biochemical process; removal of NH_3 by gas stripping	Chemical oxidants probably not appropriate.
• pH Adjustment and Buffering	Various acids and bases (nutrient acid or base such as H_3PO_4 or Na_2HPO_4)	--
• Removal of Toxic or Inhibitory Compounds	Depends on constituents to be removed	--
• Conversion of Soluble and Insoluble Organics to Organic Acids	Anaerobic fermentation with acid-forming bacteria	--
• Storage (Average of 24 hours)	Floating top tanks; flexible bag or bladder-type storage devices	It is desirable to keep the storage system anaerobic.
• Nutrient Addition	Depends on specific composition of the wastewater.	
• Feed Delivery to the Reactor	Depends on site topography, distance to reactor	Must maintain anaerobic conditions.

Table 8 (Concluded)

	Options	Comments
Hydrogen Production Area		
• Storage of Microbial Cells for Inoculum	Same as for feedstock.	Microbes may be stored along with the feedstock.
• Inert Gas Purge System for Reactor	CO_2 purge gas, N_2 purge gas, purification system off gas.	
• Photobiological Reactor	Glass or polymer tubes or pipes, glass- or polymer-covered channels, subatmospheric or pressurized operation.	
• Microbial Cell Recovery	Flocculation and sedimentation; dissolved gas flotation; centrifugation; filtration on microscreens.	
• Processing of By-Product Cells	Dewater by mechanical means (centrifugation or filtration); dry by solar means (drying beds, hot air dryers) or by conventional means using boiled flue gas or dedicated burner flue gas; steam-heated dryers.	
• Hydrogen Collection and Transmission Line	Pressurization of hydrogen at each reactor, pressurization of the hydrogen at a central point.	
Gas Processing and Storage		
• Gas Compression	Reciprocating or centrifugal compressor.	Pressure depends on gas cleaning process used.
• Gas Purification	Numerous chemical and physical absorption processes; adsorption processes; cryogenic processes; diffusion processes.	
• H_2 Storage	Pressurized storage as gas; pressurized storage as liquid; metal hydrides.	
• CO_2 Recovery and Storage	Storage under pressure as gas or liquid; storage as a solid.	
General Facility Utilities and Services	Laboratory and offices. Maintenance shop and materials storage. Roads, drainage, fences, and lighting. Fire protection. Electric power substation and distribution.	

Because we were instructed by SERI not to select a specific wastewater stream, but instead to make the analysis very general, it is impossible to specify all of the unit operations or processes that might be required. We, therefore, have analyzed a case that includes only those unit operations or processes that are likely to be required for any case. These include:

Wastewater Pretreatment and Storage
- Solids Removal (gravity sedimentation)
- Storage Tank (floating cover tank)
- Feed Delivery Pump to Reactors

Hydrogen Production Area
- Photobiological Reactor*
- Cell Mass Harvesting
- Raw Gas Collection and Transmission to Gas Processing

Gas Processing and Storage
- Gas Compression
- Gas Purification
- Hydrogen Storage

Wastestream Pretreatment and Storage

During each of the processing steps, care should be taken to eliminate or reduce the feedstock contact with air because dissolved oxygen will inhibit the anaerobic growth and hydrogen production of the hydrogen-producing organisms.

The possible substrates for photosynthetic bacteria were discussed earlier. We have assumed that the wastewater will need to be clarified by gravity sedimentation before storage. Gravity sedimentation will be accomplished using a closed top vessel to prevent oxygenation of the wastewater. The clarifier will be maintained at a constant fluid level and operate on a continuous or semi-continuous flow basis. The overflow from the clarifier will flow by gravity to a covered sump where it will be pumped to a floating top storage tank. The storage vessel will be innoculated with the harvested hydrogen-producing organisms at the end of each day. This will provide time for acclimation and some nitrogen removal during growth. The most growth may occur during the initial light hours in the reactor system and will be included in the reactor start-up time requirements.

Based on reactor design assumptions, the feed delivery pumps to the photobiological reactor will be designed to pump all of the feed from the storage tank to the reactors within a period of 120 minutes.

The solids removed from the wastewater in the clarifier will be collected and processed in an existing wastewater treatment facility assumed to already exist on the site where the wastes are generated.

Reactor Design and Operation

The design of a reactor system was specifically excluded from the scope of work for this project by Dr. Lindsey of SERI. Only some of the important design considerations are briefly discussed here. The two major options in terms of reactor morphology include various types of shallow flow channel reactors or glass pipeline reactors. Appendix A describes a design for a shallow flow channel reactor system that takes advantage of the intermittent light effect.

The reactors may be operated on a batch-fed basis (all of the substrate added at once) or on a continuous-feed basis during the 8 hours of daily operation. Based on a very cursory analysis by SRI of the two operating options (not reported here), it does not appear that the reactor volume requirements will vary dramatically for either approach.

The reactor should be operated for 6 to 8 hours per day during the maximum daylight intensity. The feedstream volume collected overnight can be discharged into the reactor during early morning hours and recirculated in the reactor until late afternoon. Once the processing time has elapsed, the biomass can be harvested and the media discharged. The reactors and other process equipment can be cleaned and serviced overnight as required.

To optimize the culture conditions for bacterial hydrogen production, one must consider the variability of light and temperature resulting from diurnal and annual cycles.

One of the major design problems with the system described is maintaining gas-tight conditions so as to prevent H_2 leaks, or air infiltration into the reactor or the media recirculation system. The control of gas leakage and of purge gas requirements prior to startup must be addressed.

Cell Mass Harvesting

Harvesting of the bacteria to obtain inocula for future cultures and to produce product biomass is an important aspect of the system design. The options listed in Table 8 include flocculation and sedimentation, microscreening, dissolved gas flotation, or centrifugation. The latter two options are very likely to be far more expensive in terms of capital investment and operating costs compared with the first two options.

Successful maintenance of filamentous bacterial cultures would permit harvesting by either microscreening or flocculation and sedimentation. Flocculation and sedimentation could also offer a selectivity for filamentous bacteria over single-cell organisms and will provide a concentrated stream of biomass for storage or for fertilizer applications. The amount of biomass harvested as product, in excess of the amount needed for inoculation, will vary with the initial nitrogen content of the feedstream. We have assumed that excess biomass production is minimal and no facilities for storage are included.

We have assumed that flocculation will occur when the cells enter a quiescent region and that the cells can be concentrated in a clarifier containing a center well for flocculation. It is assumed that no chemical addition (either divalent or trivalent metallic ions or polymers) will be required. The clarifier is designed with an overflow rate of ~ 500 gal/day/ft^2 of surface area or ~ 20 m^3/day/m^2 and a depth of ~ 4 meters. On an hourly flow basis, these values are equivalent to about 21 gal/hr/ft^2 of surface area or 0.8 $m^3/hr/m^2$. These design parameters are typical of those used for clarifiers for activated sludge treatment facilities with an influent solids content of 2.5 g/liter and an underflow solids content of between 10 and 15 g/liter (Metcalf and Eddy, 1979).

Cell mass recovery will be accomplished during a 120-minute period starting in the late afternoon. The underflow from the clarifiers is pumped directly to the feedstock storage vessel.

Hydrogen Collection and Transmission

Safety is a primary concern in the design of a system for collecting the hydrogen-rich gas and transferring it to the gas purification area. The safety precautions that apply to highly flammable gases and vapor generally apply to hydrogen. Pure hydrogen is combustible in air and oxygen over wider limits than most other gases (4-75% hydrogen). The most incendiary composition is 27-30% hydrogen in air at normal temperatures and pressures. If ignited by a flame or spark flammable mixtures in a confined space can explode, depending on the specific geometry of the enclosure. This subject is beyond the scope of this analysis and will not be discussed further. The reader is referred to NBM (1965) and NBS (1976) information on the subject. Special precautions are necessary to prevent hydrogen gas leaks from tanks and equipment. Burning hydrogen exhibits such low emissivity that small leaks may be aflame and yet not be visible.

The gas composition on a wet basis will depend on the operating temperature of the reactor. The partial pressure of water at various temperature levels is as follows:

Temperature	Vapor Pressure of Water (atmosphere)
18°C (64°F)	0.02
35°C (95°F)	0.06
60°C (140°F)	0.20
70°C (158°F)	0.31
80°C (176°F)	0.47

If the reactor operates at 70°C instead of 35°C, the volume of product gas will be about 20% greater. Also, the temperature of the liquid in the reactor and the product gas will vary during the day (and by season) unless provisions are included for holding the liquid at a constant temperature. A detailed reactor design and process optimization study is required to determine the efficiency of incorporating a temperature control system in the reactor design section.

For this analysis, it will be assumed that a thermophilic bacteria* will be used and that the maximum operating temperature will be ~ 60°C.

The gas composition will be as follows:

	Vol%	
	Dry Basis	Wet Basis
H_2	67	53
CO_2	33	27
H_2O	0	20
	100	100

The wet gas has roughly a 25% greater volume than does the dry gas. Theoretically, hydrogen requires about 2.4 volumes of air per volume of pure hydrogen for complete combustion. (This is a mixture containing about 29 vol% air, which falls into the most incendiary composition range of 24 to 30% hydrogen in air.)

To achieve a sufficient oxygen level for complete combustion of the hydrogen, the system must take in a volume of air well in excess of the total volume of wet gas. The safety of the design of the collection system must be considered in more detail, but it is beyond the scope of this effort. We have assumed that the reactors will operate under a slight positive pressure ($\leq$ 4 inches H_2O or 0.01 atm) so that any leaks will result in leakage out of gas, not infiltration of air.

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*The organisms studied by SERI thus far are not thermophillic. This assumption does not alter equipment sizing or capital costs significantly.

The gas will be collected at each reactor and blown into a main transmission line by use of low head blowers. Because reactor design is not included in the scope of this effort, it is not possible to accurately estimate the costs for a collection system. We have assumed that about 2 miles of collection piping and 100 separate blowers, one at each reactor, will be required.

Gas Compression

The reactor off-gas will be compressed to 260 psig prior to the gas purification process. The purified hydrogen gas pressure will be about 250 psig because of the pressure drop through the purification process.

There are two basic mechanical methods of increasing the pressure of a gas: (1) centrifugal compressors that reduce its volume, and increase its velocity so that the velocity energy can be converted into pressure (e.g., the radial-flow and axial-flow compressors), or (2) positive displacement machines that increase pressure by reducing volume (e.g., the reciprocating, rotary-screw, rotary-lobe, sliding-vane, liquid-piston, and diaphragm compressors).

The pressure differential and inlet capacity are the two major considerations for compressor selection. An applications chart (Woods, 1978) with the operating ranges of the above compressor types was used to select a multistage reciprocating piston compressor for this application.

The speed range of a reciprocating compressor is between 300 and 600 rpm. The machines may be driven by electric motors, internal-combustion engines, steam turbines, or steam engines. Gear reduction may be necessary depending on the drive selected. On multistage machines, intercoolers are provided between stages. These heat exchangers remove the heat of compression from the gas and reduce its temperature to approximately the temperature existing at compressor intake. Such cooling reduces the volume of gas going to the high pressure cylinders and reduces the horsepower required for compression.

For this application, the compressor will be driven by an electric motor.

Any further compression of the product gas, if required, would also be done using a reciprocating compressor. Pure hydrogen, because of its high diffusivity, is not easily compressed by centrifugal compressors. The compression ratio is on the order of 1.025; thus, more than 75 centrifugal compression stages would be needed to raise the hydrogen pressure from 200 to 1700 psig (Smith, 1970).

Gas Purification

General Considerations

Numerous methods are available for purification or upgrading of hydrogen-containing gas streams. These methods include physical or chemical absorption of impurities into a liquid, cryogenic condensation, adsorption of impurities on a solid, and diffusion techniques to remove impurities from hydrogen. In general, the purity and conditions of feed and product stream, and the scale of the operation determine the appropriate purification scheme. The availability and cost of utilities such as steam, water, fuel, and refrigeration may also affect the choice. Table 9 shows several hydrogen purification methods, which are discussed in more detail in Appendices B and C. Most systems operate on a continuous basis, 24 hours per day for 330+ days per year. In this case, however, the gas stream to be treated will be produced for an average of only 8 hours per day. The gas purification system can be designed to compress and store the raw gas for continuous processing over a 24-hour period or to process the gas as it is produced during an 8-hour period. The latter situation will require that the system have a capacity three times the capacity of the continuously operating system. An optimization study is required to firmly establish which operating schedule is preferable. We have estimated, however, that the cost of 16 to 24 hours of storage capacity (for 1 million SCFD H_2 production) for the raw

Table 9

HYDROGEN PURIFICATION METHODS

Method	Impurities Removed	Operating Conditions		Impurity Concentration		Remarks
		Temp (°F)	Press. (psi)	Feed	Product	
Absorption						
Caustic scrubbing	CO_2, H_2S, SO_2, COS	Below 120	Up to 1000	Below 1%	A few ppm	Spent solvent is wasted.
Ethanolamine scrubbing	CO_2, H_2S, SO_2	≃ 100	Up to 1000	Above 3%	10 to 50 ppm	Solvent is regenerated by heating.
Hot potassium carbonate scrubbing	CO_2, H_2S, SO_2, COS	Above 230	Above 100	Above 3%	0.5 to 2%	Solvent is regenerated by pressure lowering.
Methanol scrubbing	CO_2, H_2S, SO_2, COS, C_2H_2	Below -20	300 to 1800	Above 10%	CO_2 below 100 ppm H_2S & COS below 1 ppm	Selective separation of CO_2 and H_2S is possible.
Water scrubbing	CO_2, H_2S, SO_2	Below 100	Above 300	Above 3%	About 1%	There is generally no solvent recycle.
Sodium-in-ammonia	O_2, CO_2	Below -30	Up to 1800	A few %	Trace	Ammonia is recovered by evaporation.
Adsorption						
Molecular sieves	CO, CO_2, N_2, CH_4, H_2O, C_2H_4, NH_3	40 to 100	Above 100	Below 40%	Below 10 ppm	Molecular sieve is regenerated by pressure reduction.
Cryogenics						
Liquid methane scrubbing	CO, hydrocarbons	-300	650	Below 40%	CO below 1 ppm CH_4 below 1%	Carbon monoxide can also be separated by condensation at -325°F and 300 psig.
Liquid nitrogen scrubbing	CO, Ar, CH_4	-320	650 to 2100	Below 40%	A few ppm	Hydrogen may contain up to 25% N_2 for NH_3 synthesis.
Condensation, freeze out methods	CO, Ar, N_2	-430	0 to 1500	Any	A few ppm	
Conversion						
Methanation	CO, CO_2	450 to 700	Above 100	Below 5%	A few ppm	Carbon oxides are hydrogenated to methane.
Diffusion		400 to 1200	100 to 650	Below 40%	A few ppm	Palladium is often alloyed with silver.
		100	500 (diff.)	Below 50%	Above 90%	This is Du Pont's Permasep® Process.

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*CO_2, CO, H_2S, SO_2 and COS are considered to be acid gases.

product gas is likely to be comparable to or greater than the potential investment cost savings to accrue from reducing the gas processing train capacity. We have therefore assumed that the gas processing train will operate only 8 hours per day. In selecting a process, it will be necessary to consider the case of startup and shut down of the system plus the potential energy input associated with heating or cooling of absorbents during startup. Based on a number of factors mentioned in Appendices B and C or discussed below, it has been decided that chemical absorption, physical absorption, and adsorption are the most attractive options for this application.

Comparison of Selected Absorption and Adsorption Processes

Absorption processes are typically used for treating low purity hydrogen streams. Several absorption processes are applicable to a low volume system, including chemical absorption systems such as the Benfield hot activated potassium carbonate process, or various amine systems (MEA-monethanolamine, DEB-diethanolamine), and physical absorption systems such as the water scrubbing or organic solvent processes.

Absorption--with hot alkali solutions, ethanolamine, or methanol--is probably the most widely used method for hydrogen purification. It is generally economic for higher concentrations of acid gas impurities. These processes are capable of reducing the total impurity concentration to 1% or less. The solvents are regenerated by raising their temperature or reducing their pressure to release the absorbed impurities. Absorption temperatures are on the order of -30 to 100°F and pressures are above 10 atm. The ethanolamine processes are ideally suited for the treatment of natural, refinery, and synthesis gases that contain hydrogen sulfide and carbon dioxide (acid gases) as the only impurities to be removed. Amine processes require substantial heat requirements for solvent revivication.

The cost of removing acid-gas impurities by heat regenerable absorption processes may constitute a substantial portion of the energy value of the treated gas. The heat requirement for solvent revivication of an amine-based chemical absorption process is between 80,000 and 100,000 Btu per lb mole of CO_2 absorbed (Piel, 1980). This heat requirement is equivalent to 100 to 125 MM Btu/10^6 SCFD H_2 or 37 to 46% of the energy recovered as hydrogen in the product gas stream. Energy is also required for solvent recirculation and cooling water pumping.

The activated Benfield Process, another chemical absorption process, requires about 30,000 to 40,000 Btu/lb mole CO_2 or 14 to 19% of the energy recovered as hydrogen. Operating costs for pumping must also be included for this process.

In contrast, the operating energy requirements for a molecular sieve adsorption system are quite small. However, the recovery efficiency may range between 60 and 90%. Assuming a typical H_2 recovery value of 75%, or a loss of 25%, the adsorption process compares well with the activated Benfield Process on an energy recovery basis (if H_2 is used as a fuel in the Benfield process). However, for a small-scale facility (~ 1 MM SCFD H_2), the capital costs of a physical absorption process or molecular sieve adsorbent processes are lower than that for the chemical absorbent systems.

Physical Absorption Systems

The economic disadvantages of heat-regenerable absorbent processes may be overcome by processes based on the use of organic solvents, which physically dissolve the acid gases and can be stripped by reducing the acid-gas partial pressure without the application of heat.

The physical absorption processes require a high partial pressure of acid gas in the feed gas to achieve higher loading than the chemical absorbent processes. To be practical, the solvents must have a high selectivity for CO_2 over H_2, a very low vapor pressure at ambient temperature to reduce vaporization losses, a low viscosity to reduce pumping costs, noncorrosiveness to common metals, and be nonreactive with CO_2, H_2O or H_2. Since physical solvent processes are most efficient when operated at the highest possible pressure, carbon dioxide removal from gases such as reformer effluents is best performed after the gas is compressed to the ultimate pressure required for such processes as ammonia synthesis (150 atm) or hydrocracking (50-170 atm).

Physical organic solvent processes are most economical for bulk removal of acid-gas contaminants. When high-purity treated gas is required, solvent regeneration methods beyond simple flashing are used.

The five major processes using physical solvents in commercial operation are Fluor solvent, Purisol, Selexol, Estasolvan, and Sulfinol. All of these processes are quite similar, differing only in the solvent selection.

Physical solvent processes require little more than an absorber, atmosphere flash vessel, and solvent recycle pump. No steam or heat source is required. For bulk removal of acid gases, a split stream cycle with partially stripped solvent is used, followed by final purification with completely regenerated solvent. The absorber solvent may be flashed at two or three pressure levels to remove dissolved nonacidic gases that are recompressed and returned to the absorber inlet. If product gas of high purity is required, the residual acid-gas content of the solvent is further reduced by stripping with air or an inert gas.

For large-capacity plants, the rich solvent and the flashed acid gases are frequently expanded through power recovery turbines. Since the absorption capacity of the physical solvents increases as the temperature is lowered, it is advantageous to operate at the lowest possible temperature.

The Fluor solvent process uses propylene carbonate as the physical solvent. Physical and solubility properties of propylene carbonate are given in Table 10. The selectivity of propylene carbonate for CO_2 over H_2 (120:1) makes this solvent ideal for treatment of synthesis gas for the production of ammonia and urea by steam reforming of natural gas and naphtha by partial oxidation. Cook and Tennyson (1969) concluded that propylene carbonate absorption is more economical than activated hot potassium carbonate for feed rates of 10-20 MM SCFD. CO_2 feed composition of 17-23%, and absorption pressures of 450-800 psig. At lower pressures, the CO_2 solublity in physical solvents is less. Thus, the physical solvent systems may be economical if the product gas use requires high pressure hydrogen. If the product gas pressure requirement is below 250 psig, the higher solvent recirculation rates and larger capital costs of an absorbent system may favor the molecular sieve adsorption process.

The inlet contaminated gas will still contain water vapor, although the majority is removed during compression. This water will accumulate in the initially anhydrous organic solvent. A portion of the physical solvent (sidestream) must then be distilled continuously to remove the absorbed water.

Table 10

PHYSICAL AND GAS SOLUBILITY PROPERTIES OF PROPYLENE CARBONATE (P.C.)*

Empirical formula	$C_4H_6O_3$
Molecular weight	102.1
Viscosity, 35°C	~ 2 centistokes
Boiling point, 760 mm Hg	240°C
Vapor pressure, 35°C	0.12 mm Hg
Heat of vaporization, 240°C	458 Btu/kg
Heat of solution-saturation with CO_2, 26°C	1.5 Btu/kg
Solubility of CO_2, 25°C, 1 atm	3.6 vol. CO_2/vol. P.C.
Solubility of H_2, 25°C, 1 atm	0.03 vol. H_2/vol P.C.

Adsorption Technology

Adsorption techniques are usually best suited for treating small volumes of fairly pure hydrogen. The low capacity of adsorbents for some impurities can require large volume systems and, where the impurity concentration or quantity is large, appreciable loss of hydrogen can occur with the revivification of the adsorbent.

Hydrogen impurities such as CO, CO_2, CH_4 C_2H_4, N_2, NH_3, and H_2O are adsorbed from hydrogen gas at normal temperatures and at pressures of 200 psig or higher by zeolite molecular sieve adsorbents in a pressure swing cycle. The purity of the hydrogen passing through the adsorbent bed may be as high as 99.999%.

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*From Dow Chemical of Canada Ltd., 1962 Gas Conditioning Fact Book.

Discontinuing the hydrogen flow and dropping the pressure by 200 psig releases the adsorbed impurities. Because of the use of pressure reduction to desorb impurities, these systems are commonly called pressure swing adsorption (PSA). The hydrogen yield is generally in the range of 60 to 90% of that in the feed. Four automated adsorption beds in parallel--for adsorbing, depressurizing, purging, and repressurizing, respectively,--give an essentially continuous flow of purified hydrogen.

PSA units may use either a 4-bed system or a more advanced 10-bed system. The 4-bed systems usually have one bed for adsorption while the other 3 beds are undergoing various stages of regeneration. All systems use a void gas recovery technique* to provide maximum product recovery. An additional feature of PSA is that all impurities are removed in a single step and ultrahigh purities are obtainable irrespective of the number or concentration of the impurities.

All the PSA units are completely automatic and can be left unattended after startup. Startup and shutdown are push-button operations. After initial startup the unit can at once begin operating at full load. Turndown capabilities are as low as 5%, thus emphasizing flexibility. All units are completely built and skid-mounted. Installation and adsorbent loading are simple and easy. The units are designed for outdoor operation and require only small quantities of instrument air and power.

The operating economics are mainly determined by equipment maintenance and feed gas compression costs because no utilities are required. Costs can be partially offset by the fuel value of waste gas. The following tabulation shows the effect of size (economies of scale) when treating a feed containing 90% H_2 at 250 psig based on a three-year writeoff, a feed value of \$2.00/1000 ft^3, and a fuel value of \$1.50/1000 ft^3 (Hydrocarbon Processing, 1979).

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*The gas occupying the void space will contain a significant amount of H_2. Once breakthrough occurs, a saturated bed can be used to repressurize a regenerated bed. Thus, a portion of the H_2 can be recovered.

Product Rate (MM SCFD)	H_2 Purification Cost (¢/1000 ft^3)
1	61
10	27
50	20

For this preliminary analysis, we feel that a PSA gas purification system is a reasonable choice, even though we have assumed that the acid gas (CO_2) content is relatively high. The major reasons for choosing a PSA system are as follows:

- It is simple to operate (ease of startup, shutdown, and noncontinuous operation).
- It is flexible with respect to temperature, pressure, and turndown capability.
- The hydrogen losses (as energy equivalent) due to inefficient separation are comparable to the heat requirements for an absorption process.
- It requires negligible energy for operation, whereas the pumping requirements for solvent processes may be significant.
- A number of PSA systems are now in operation for removal of CO_2 from landfill gases that contain up to 50 vol% CO_2 (on a dry gas basis) and gas volumes in the range of one to several million SCFD.

A detailed comparison of PSA with physical absorption processes should be done in the future. A PSA unit that would be suitable for this application is available from the Union Carbide Corp., Linde Division, NJ or AIRCO Industrial Gases, NJ.

Hydrogen Storage

Hydrogen may be stored by the following means:

- As a gas under pressure
- As a liquid at low temperature
- As a metal hydride.

The first two options are now in widespread commercial use. The specific methods of storage will depend to a great extent on the end use. For this analysis we have assumed that the hydrogen is stored as a gas under pressure. The volume of purified hydrogen gas produced per day is ~ 0.773 MM SCF or 2.2×10^4 SCM. The high pressure gas will occupy a smaller volume determined by the pressure ratio as $0.773 \times 10^6(15 \text{ psia}/270 \text{ psia}) = 4.3 \times 10^4 \text{ ft}^3/\text{day}$ or $1.2 \times 10^3 \text{ m}^3/\text{day}$; assuming a storage capability equivalent to one day's production volume and a 15% excess capacity gives the storage vessel volume as $\sim 1400 \text{ m}^3$ or $\sim 5 \times 10^4 \text{ ft}^3$.

Materials of Construction

The materials of construction used in a hydrogen plant may be subject to carbonyl formation, erosion, corrosion from acidic condensates, salts and H_2S, and hydrogen embrittlement (Harnby, 1966).

The problems of hydrogen embrittlement can become critical to the application of lightweight, high strength steels and alloys at high temperatures or pressures, neither of which will be experienced at the subject facility. No problems should be expected from the use of ordinary carbon steels.

For further information, the reader is referred to an extensive set of graphs by Nelson (1965) showing the life of various steels in hydrogen at different temperatures and pressures.

SUMMARY OF PROCESS DESIGN ASSUMPTIONS AND EQUIPMENT SIZING

Design Bases

2.83×10^4 M^3/day (10^6 SCFD) of hydrogen (gross output)

Feedstream substrate concentration of 2.5 gm/L

No pH adjustment required, pH ≅ 7

Feedstream temperature of ~ 100°F ≡ 38°C

23.6 metric tons of substrate required per day

Nitrogen concentration below 200 mg/L

12 hr/day plant operation

8 hr/day gas production

Preclarification

Assume existing clarifier is used, reducing suspended solids to below 40 mg/L

Storage Tank

Covered floating-top tank, 24-hour capacity
85% of working volume used

Total vessel volume ≅ 1.1×10^7 liters (~ 3×10^6 gallons)

Pumps from storage to reactor system*

Large volume, low head, low shear pump

Archimedes-type screw pumps pumping 9.5×10^6 liters in 2 hr with 5-m lift

Reactor System

50 acres (~ 20 hectares) of covered shallow channels operating at 10 to 15 cm of H_2O pressure

100 separate reactors 5 cm deep, 120 m long, and 15 m wide

50 Archimedes-type screw pumps operating with a 5-m lift

8 hr of operation/day

Operating temperature of 60°C

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*Design will depend on reactor design assumptions.

Clarifier for Cell Mass Recovery

Covered tanks

8×10^4 L/min total flow rate for 2 hr

4 clarifiers each at 2×10^4 L/min flow rate

Clarifier overflow rate = 14 L/min/m^2 (500 gal/day ft^2)*

2×10^4 L/min/14 L/min/m^2 = 1400 m^2 of surface area per clarifier.

Area = $\pi D^2/4$ = 1400 m^2, $D \cong 42$ m (diameter), 4-m deep.

Underflow concentration of 10 g solids/L.

95% solids recovery gives combined underflow volume as 2.24×10^6 L/2 hr or 1.12×10^6 L/hr.

The underflow stream is pumped to thickeners at a at a flow rate of 1.12×10^6 L/hr and a concentration of 10 g/L (1.12×10^4 kg/hr of solids)

Design solids loading for thickener is ~ 45 kg/m^2/day or 1.875 kg/m^2/hr.

Surface area of the thickeners is 1.12×10^4 kg/hr/1.875 kg/m^2hr $\doteq$ 6000 m^2.

Each thickener has a surface area of 6000/4 $\cong$ 1500 m^2 and a diameter of 44 m.

The underflow concentration will be 50 g solids/L.

At 95% solids recovery, the underflow volume is then 4.25×10^5 L/2 hr or 2.1×10^5 L/hr

The underflow stream from the thickeners is pumped to the feedstream storage vessel.

Gas Collection†

100 blowers operating with a pressure differential of 1/3 atm, each pumping 66.5 m^3/hr (2.35×10^3 SCF/hr)

8 hr of operation/day

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*From Metcalf & Eddy (1979).

†Design will depend on reactor design assumptions

Gas Compression

Three-stage reciprocating compression, initial pressure of 1/3 atmosphere (gauge)

Interstage cooling including removal of ~ 95% of water content

Final pressure ~ 18 atm (gauge),

Initial temperature ≐ final temperature ≤ 60°C,

8 hr of operation/day

Final water vapor pressure < 3 psia.

Gas Purification

Molecular sieve adsorption system (PSA 4 bed unit)

8 hr of operation/day,

Capacity ≡ 22 kg CO_2/100 kg adsorbent

Density ≡ 800 kg adsorbent/m^3,

Void volume ≅ 25%

Total bed volume = 9000 ft^3 or 250 m^3

Each bed in a 4-bed system on a 1-hr cycle is 1125 ft^3 or 32 m^3

Final hydrogen purity ≡ 97%, CO_2 ≡ 3%, trace H_2O

Hydrogen Storage

High pressure gas, 255 psig

1 day design capacity

15% excess capacity

Total storage volume = 1400 m^3 or 5 x 10^4 ft^3

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*Design will depend on reactor design assumptions.

APPROXIMATE MASS BALANCE

A mass flow sheet for a hydrogen production facility was constructed with the assumptions discussed in the previous sections. The five basic operations are shown in Figure 2. The feedstream is assumed to contain 23.6 metric tons of substrate in approximately 10^7 liters per day. Assuming a substrate consumption factor of 0.8 gives, by stoichiometry, 1.5 MM SCFD of dry gas (66% H_2 and 33% CO_2). The wet gas at 60°C will contain approximately 0.38 MM SCFD of water, giving a total gas volume of 1.88 MM SCFD (36.9 metric tons/day). After the 7-hour process time, the circulation pumps are stopped and the media (containing 23.8 metric tons of cells) are passed through a clarifier. The underflow from the clarifier (concentration of 10 g/liter) can be thickened to produce a solids content of 5% (50 g/L). These operations are assumed to recover up to 90% of the cell mass* (21.2 metric tons dry wt of cells). The split between cell mass for storage and product biomass can be determined once a nitrogen content of the feedstream is specified.

The 36.9 metric tons/day of untreated wet gas is compressed to 260 psig and cooled to 60°C. Approximately 95% (8.87 metric tons) of the water vapor in the gas will condense during this operation, giving 1.52 MM SCFD of gas of about 1 mole percent water. The remaining 30 metric tons of untreated gas is processed in a PSA purification system. The hydrogen recovery factor is assumed to be 0.75, giving a purified hydrogen stream of 0.773 MM SCFD at 97 vol% H_2 and 255 psig. The dilute fuel gas from the purification system will contain approximately 34 vol% H_2 and 65 vol% CO_2 (27.1 metric tons/day).

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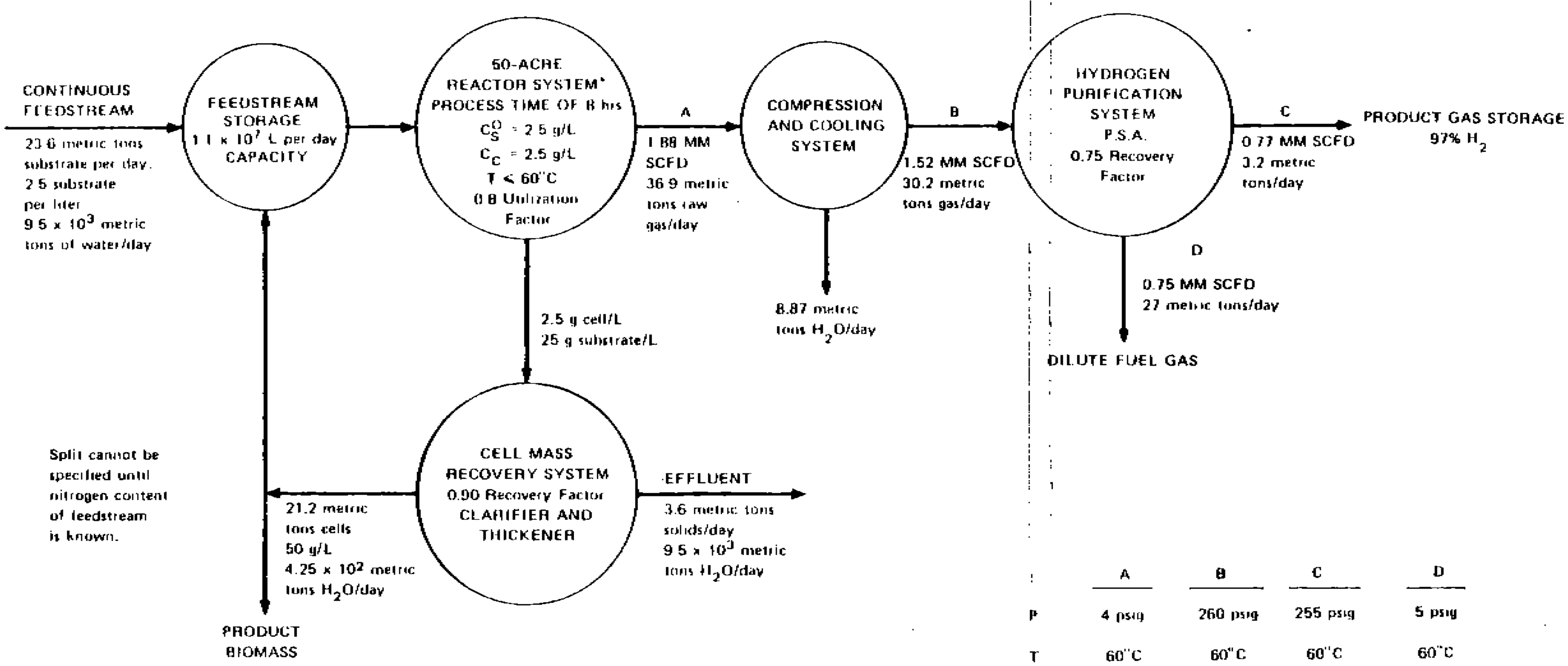
*Gravity sedimentation without the aid of a flocculating agent may not be feasible because of flotation of cells from gas production in the clarifier.


CONTINUOUS FEEDSTREAM
23.6 metric tons substrate per day.
2.5 substrate per liter
9.5 x 10³ metric tons of water/day
FEEDSTREAM STORAGE
1.1 x 10⁷ L per day CAPACITY
50-ACRE REACTOR SYSTEM*
PROCESS TIME OF 8 hrs
C_S^O = 2.5 g/L
C_C = 2.5 g/L
T < 60°C
0.8 Utilization Factor
A
1.88 MM SCFD
36.9 metric tons raw gas/day
COMPRESSION AND COOLING SYSTEM
8.87 metric tons H_2O/day
B
1.52 MM SCFD
30.2 metric tons gas/day
HYDROGEN PURIFICATION SYSTEM
P.S.A.
0.75 Recovery Factor
C
0.77 MM SCFD
3.2 metric tons/day
PRODUCT GAS STORAGE
97% H_2
D
0.75 MM SCFD
27 metric tons/day
DILUTE FUEL GAS
2.5 g cell/L
25 g substrate/L
CELL MASS RECOVERY SYSTEM
0.90 Recovery Factor
CLARIFIER AND THICKENER
EFFLUENT
3.6 metric tons solids/day
9.5 x 10³ metric tons H_2O/day
21.2 metric tons cells
50 g/L
4.25 x 10² metric tons H_2O/day
Split cannot be specified until nitrogen content of feedstream is known.
PRODUCT BIOMASS

	A	B	C	D
P	4 psig	260 psig	255 psig	5 psig
T	60°C	60°C	60°C	60°C
Mole H_2%	53	66	97	34
CO_2%	27	33	3	65
H_2O%	20	1	Traces	1

MASS BALANCE†

SUBSTRATE CONSUMED	18.9	HYDROGEN PRODUCED	2.5
WATER CONSUMED	11.3	CARBON DIOXIDE PRODUCED	27.7
	30.2 metric tons/day		30.2 metric tons/day

*Water Consumed by Reaction $n(CH_2O) + nH_2O \rightarrow nCO_2 + 2nH_2$ is < 0.03 metric tons/day

† Neglecting Cell Mass

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FIGURE 2 MASS FLOWSHEET FOR 1 MM SCFD HYDROGEN PRODUCTION FACILITY

APPROXIMATE ENERGY BALANCE AND SUMMARY OF MAJOR UTILITY AND OPERATING REQUIREMENTS

An energy flow sheet was constructed with the assumptions discussed in the previous sections. The five basic operations are shown in Figure 3. The feedstream is assumed to contain 23.6 metric tons of substrate in approximately 10^7 liters. The heat of combustion of a CH_2O equivalent is about 110 kg calories/mole. This gives the substrate energy input as

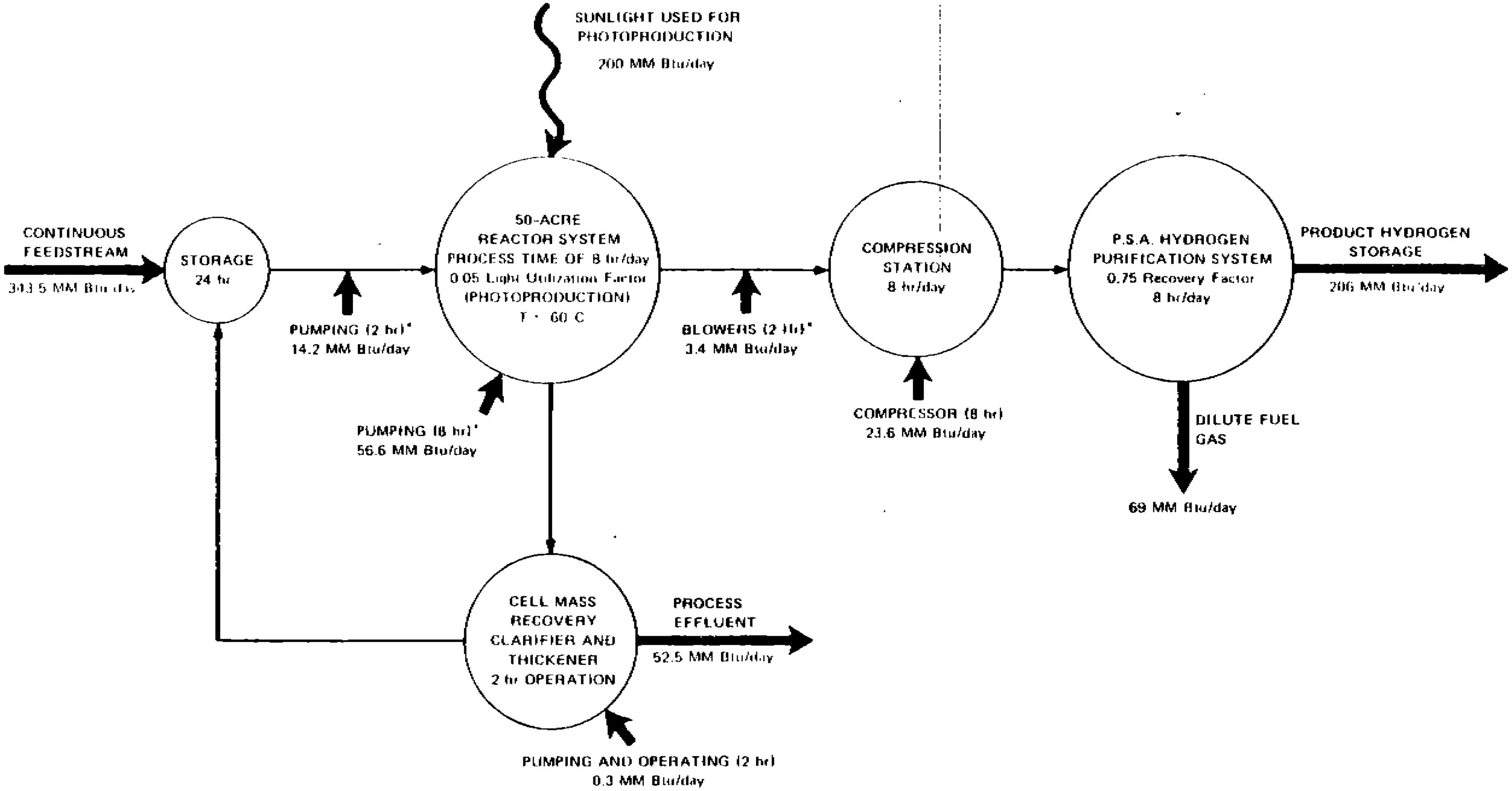
$$23.6 \times 10^6 \text{ g } \frac{CH_2O}{\text{day}} \cdot \frac{\text{Mole}}{30 \text{ g } CH_2O} \cdot \frac{3.97 \text{ Btu}}{\text{kg calorie}} \cdot \frac{110 \text{ kg calorie}}{\text{Mole}} =$$

$$343.5 \text{ MM } \frac{\text{Btu}}{\text{day}} = 86.5 \text{ MM kg } \frac{\text{calories}}{\text{day}}$$

The pumping energy requirement for delivery of the feedstream to the storage vessel has been ignored. The pumps required to fill the reactors are assumed to operate for 2 hours at 5×10^6 liters/hr overall flow rate and $\sim$ 5 m head and will require 4150 kWh (14.2 MM Btu) (see Appendix A). The recirculation pumps in the reactor system will operate for 8 hours against $\sim$ 5 m head in each of the fifty 1-acre, reactors. The power requirement is then 41.5 kW/pump (8 hr) (50 pumps) = 16600 kWh (56.6 MM Btu) (see Appendix A).

The reactor offgas will need to be collected in a duct system and delivered to the gas compression station. It was assumed that 100 blowers are operating, one at each channel (50 acres, 2 channels per acre). The gas flow rate is about 1.9×10^6 SCFD for 8 hours. A correlation from Perry (1973) was used to calculate the power requirement as follows:

$$\text{Shaft Horsepower} = \frac{144 \; Q \; \Delta p}{33{,}000 \text{ efficiency}}$$


SUNLIGHT USED FOR PHOTOPRODUCTION
200 MM Btu/day
CONTINUOUS FEEDSTREAM
343.5 MM Btu/day
STORAGE
24 hr
PUMPING (2 hr)*
14.2 MM Btu/day
50-ACRE REACTOR SYSTEM
PROCESS TIME OF 8 hr/day
0.05 Light Utilization Factor
(PHOTOPRODUCTION)
T · 60 C
PUMPING (8 hr)*
56.6 MM Btu/day
BLOWERS (2 Hr)*
3.4 MM Btu/day
COMPRESSION STATION
8 hr/day
COMPRESSOR (8 hr)
23.6 MM Btu/day
P.S.A. HYDROGEN PURIFICATION SYSTEM
0.75 Recovery Factor
8 hr/day
PRODUCT HYDROGEN STORAGE
206 MM Btu/day
DILUTE FUEL GAS
69 MM Btu/day
CELL MASS RECOVERY CLARIFIER AND THICKENER
2 hr OPERATION
PROCESS EFFLUENT
52.5 MM Btu/day
PUMPING AND OPERATING (2 hr)
0.3 MM Btu/day

ELECTRICITY UTILIZED*	98
SUBSTRATE CONSUMED	291
SUNLIGHT UTILIZED	200
MAJOR ENERGY INPUT	589 MM Btu/day

*May Depend on Reactor Design Assumptions

PRODUCT GAS	206
DILUTE FUEL GAS	69
	275 MM Btu/day
UNUTILIZED SUBSTRATE	52
OTHER LOSSES (HEAT)	262
MAJOR ENERGY OUTPUT	589 MM Btu/day

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FIGURE 3 MAJOR ENERGY INPUT AND OUTPUT FOR 1 MM SCFD HYDROGEN PRODUCTION FACILITY

where $Q \equiv$ volumetric flowrate, ft^3/min

$\Delta p \equiv$ developed head, psi

Blower efficiency = 60%, motor efficiency = 85%

Assuming a 5-psi head, and a gas flow rate of

$$1.9 \times 10^6 \text{ SCF/day} \left(\frac{\text{day}}{24 \text{ hr}}\right)\left(\frac{\text{hr}}{60 \text{ min}}\right) = 1.3 \times 10^3 \text{ SCFM}$$

Given 8 hours of operation, the specific flow rate is

$$\frac{24}{8} \; 1.3 \times 10^3 \cong 4 \times 10^3 \text{ SCFM}$$

$$P = \frac{144 \cdot 0.4 \cdot 10^3 \cdot 5}{33{,}000 \cdot 0.85 \cdot 0.60} = 168 \text{ hp}$$

0.7457 kW/hp (168 hp) = 125 kW

Operation for 8 hours then requires 1000 kWh (3.4 MM Btu). Operating energy requirements for the calrifier and thickener operations are estimated to be ~ 55 kWh/day (0.19 MM Btu/day). Gas compression will require 9300 hp hr/day (Appendix D) or 6935 kWh/day (23.6 MM Btu/day). The total electrical energy requirement is then 28770 kWh/day (98 MM Btu/day).

Assuming a 0.8 substrate utilization factor gives the remaining substrate heating value in the process waste as 69 MM Btu. Assuming that 25% of this remaining substrate was converted to cell mass that was recovered in the clarifier gives ~ 52 MM Btu of CH_2O material in the process waste stream after clarification.

The gas purification section produces two hydrogen streams, one at 0.77 MM SCFD and 97% H_2, giving 206 MM Btu/day (275 Btu/SCF) and another at 0.75 MM SCFD and 34% H_2, giving 69 MM Btu/day.

The solar energy input to the system can be found assuming 3×10^{10} Btu/acre/yr for insolation and a 50-acre reactor surface area. This gives the solar input as

$$3 \times 10^{10} \text{ Btu/acre/yr} \cdot 50 \text{ acres} \cdot \frac{\text{yr}}{365 \text{ days}} = 4 \times 10^9 \text{ Btu/day}$$

A majority of this energy is lost by reflection or is absorbed as heat. Assuming that the solar energy conversion efficiency for H_2 production is about 5% gives the energy utilized as 200 MM Btu/day.

The above discussion has neglected the energy requirements for preheating and temperature control of the reactor, the cooling requirements of the compressor operation, the heat absorbed in the reactor from sunlight, and heats of reaction.

There are various wasy to calculate the efficiency of the process. Three different approaches are described below:

(1) Total balance, including actual solar energy used and assuming purchased electric power at 3414 Btu/kWh and a heating value of 14.6 Btu/g for the soluble substrate [(275/589) x 100 = 47%].

(2) Total balance as above, but assuming purchased electric power at 10,000 Btu/kWh, at 34% overall efficiency for generation and delivery (275/778 · 100 = 35%).

(3) Ratio of hydrogen output to electric power input using 3414 Btu/kWh and 10,000 Btu/kWh (275/98 = 2.8; 275/288 = 0.95)

The dilute fuel gas from the purification section can be used for steam production. The gas contains approximately 69 MM Btu/day at a flow rate of 0.75 MM SCF/day. The gross heating value (Btu/ft^3) is then 69 x 10^6 Btu/0.75 x 10^6 ft^3 or 92 Btu/ft^3. This is equivalent to that of blast furnace gas. Assuming a flue gas exit temperature of 600°F (315°C), the efficiency of combustion defined as available heat/gross heating value is ~ 80% (North American Manufacturing Co., 1952). Thus, only 55 MM Btu/day of energy is recoverable from the dilute fuel gas stream during combustion. To produce electricity, and overall thermal efficiency of ~ 25% could be expected. This gives ~ 15 MM Btu/day as electrical power produced, whereas ~ 100 MM Btu/day are estimated for operation.

ECONOMIC BASES

The economic bases used for our analysis including capital investment, operating and maintenance costs, financial assumptions and plant construction and operating schedules--are summarized in Table 11.

Table 11

ECONOMIC BASES FOR HYDROGEN PRODUCTION
(Fourth Quarter 1980 U. S. Dollars)

(Base-Case Plant Capacity = 1 MM SCFD)

Capital Investment Assumptions	
General Services Facilities	5% of other PFI*
Royalties	Not included
Land	$5,000 per acre
Materials Inventory	Negligible
Organization and Start-Up Exprense	5% of PFI
Operating and Maintenance Cost Assumptions	
Purchased Power	3.5¢/kWh
Direct Operating Labor Rate	$10.0 per hour
Maintenance Labor	1% of PFI
Supervision	15% of operating labor
Administrative Support	20% of operating and maintenance labor
General Administrative Expense	2% of PFI
Payroll Burden	35% of all labor
Maintenance Materials	1% of PFI
Property Tax and Insurance	2.5% of PFI
Stream Factor†	45%

Table 11 (Continued)

Financial Assumptions

Industrial, Nonregulated Financing	100% equity with 15% DCF[‡] rate of return
Project Life	20 yr
Depreciation Period	15 yr
Depreciation Method	Sum of years digits
Income Tax	50%
Investment Tax Credit	10% and 30%

Plant Construction, Start-up, and Operating Schedule Assumptions (percent)

Start of Year	Depreciable Investment, 2-Year Construction	Purchased Land	Revenue
1	-25%	100%	--%
2	-75	--	--
3 (1st yr of start-up)	--	--	70
4 (2nd yr of start-up)	--	--	100

---

[*] Plant facilities investment

[†] Assuming 12 hours of labor and operation including start-up, shutdown, and 8 hours of hydrogen production. (12 hr/day) 365 (0.9) days/yr = 3940 hr/yr. 24 hr/day 365 day/yr = 8760 hr/yr. 3940/8760 = 0.45.

[‡] Discounted cash flow.

CAPITAL INVESTMENT AND OPERATING COSTS ESTIMATES

The capital cost estimates for each major unit operation of a hydrogen production facility are shown in Table 12. All equipment cost estimates (e.g., pumps, storage vessels) have been estimated from Guthrie (1969). The reactor cost estimated is $\$8/ft^2$, which is comparable to the estimate given by Burford (1977) for a 6-acre algae culture system with a non-gas-tight cover. The choice of $\$8/ft^2$ for this situation is artibrary. A range in the reactor cost of \$4 to $\$20/ft^2$ was used to illustrate the effect on revenue requirements of changes in the reactor cost. The costs for a clarifier and thickener were estimated from Dahlstrom (1971). Note that the reactor cost estimate of $\$8/ft^2$ constitutes 70% of the total plant facilities investment of \$25 million.

For comparison, a rough estimate of capital cost for a glass pipe reactor system was made from information provided by Paul Hands at Matheson Doherty Co. of San Francisco (a representative of Corning Glass Works). The estimates of \$29/linear ft of 6-inch diameter pipe and \$100/linear ft of 18-inch diameter pipe included pipe joints and supporting structure, but did not include site preparation or pad installation and cost. Assuming a total system liquid volume of 10 liters gives the reactor capital cost as \$52 million for 6-inch diameter pipe and \$20 million for 18-inch diameter pipe. These estimates did not include recirculation pumps or gas collection ductwork. This cost is higher than the highest reactor cost mentioned for the cost sensitivity analysis.

Table 13 presents the estimated total annual operating costs and revenue requirements for a 1 MM SCFD facility with the assumptions presented in the text. In this analysis the feedstock purchase price was ignored since no specific wastestream or site was chosen. The effect of feedstock cost or credit may or may not be substantial.*

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*The possibility exists that a fee would be paid to process and treat the effluent stream; this would lead to a reduced total revenue requirement.

Table 12

ESTIMATED TOTAL CAPITAL INVESTMENT FOR HYDROGEN PRODUCTION
(Millions of Dollars)

(Basis: Production of 10^6 SCF Hydrogen per day)

Plant Facilities Investment	Amount
Raw material receiving, preparation, and storage[*]	$ 1.2
Delivery pumps[†]	0.1
Reactors[†]	17.5
Clarifier and thickener (cell mass recovery)	2.0
Gas purification	2.0
Hydrogen Storage	1.0
General service facilities, 5% of other PFI	1.2
Total PFI[†]	25.00
Capital Investment	
Land	0.36
Organization and Start-up Expenses	1.25
Interest During Construction	2.69
Working Capital	0.21
Total Capital Investment[*]	29.51

---

[*] An alternative feedstream storage container is the Modutank offered by pca Industries Inc. (Long Island, NY). This container is an uncovered modular tank with a flexible membrane liner. The FOB cost for this container would be about $180,000 ($10^7$-liter capacity). These containers require low construction time and little land preparation; however, they provide no means of reducing airborne bacterial contamination or oxygenation of the collection wastestream.

[†] Will depend on reactor design assumptions.

Table 13

ESTIMATED ANNUAL OPERATING COSTS AND REVENUE REQUIREMENTS FOR PRODUCTION OF 1 MM SCFD OF HYDROGEN

	Millions of Dollars per Year	Dollars per Million Btu	Dollars per 1000 SCF
Materials and supplies (M and S)			
Feedstock	0	0	0
Chemicals	0	0	0
Electric Power*	0.28	4.11	1.13
Maintenance materials	0.25	3.67	1.01
Total M and S	0.53	7.78	2.14
Labor			
Operating labor (1 man/shift)	0.09	1.32	0.36
Supervision	0.01	0.15	0.04
Maintenance labor (1 man/shift)	0.25	3.67	1.01
Administrative and support labor	0.07	1.03	0.28
Payroll burden	0.15	2.20	0.61
Total labor	0.57	8.37	2.30
Fixed Costs			
G and A expenses	0.5	7.35	2.02
Property taxes and insurance	0.62	9.11	2.50
Total fixed costs	1.12	16.46	4.52
Total annual operating costs*	2.22	32.62	8.97
Capital-related charges and income tax†	6.58	96.67	26.59
Total revenue requirement*	8.80	129.29	35.56
Sources of required revenue			
Hydrogen	8.80	129.29	35.56

---

[*] May depend on reactor design assumptions

[†] Depreciation included.

Figure 4 presents the estimated revenue requirements for production of 1000 SCF of H_2, given the plant facility investment costs as \$15, \$25, and \$50 million. For a base case plant facilities investment of \$25 million, the revenue requirement is \$35.5/1000 SCF (Table 13). This cost is several times the current bulk price of ~\$10/1000 SCF.

It appears that the reactor investment cost will be a major factor in determining the economics of hydrogen production by photosynthetic bacteria. The estimated reactor cost is 70% of the total base case plant facilities investment. Thus, the reactor design and operation warrant a more detailed investigation.

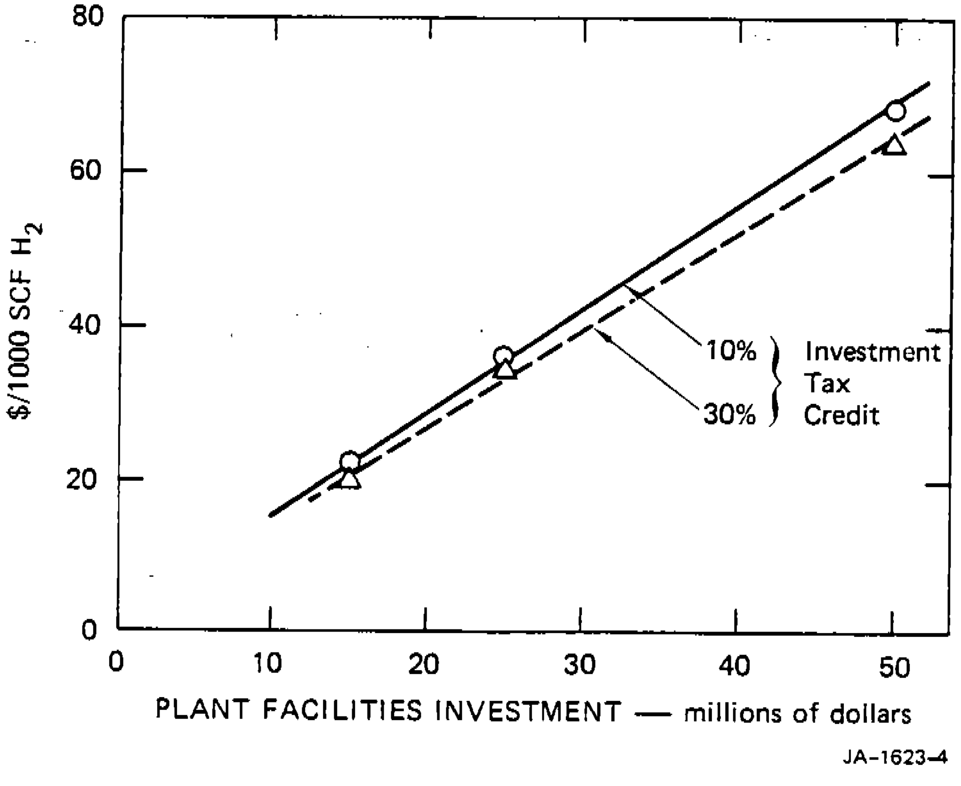


FIGURE 4 REVENUE REQUIRED VERSUS PLANT FACILITIES INVESTMENT COST (Basis 1 MM SCFD Hydrogen)

Appendix A

PROPOSED SHALLOW FLOW CHANNEL SYSTEM

The Intermittent Light Effect and Light Utilization

Researchers have long recognized that the dark reactions of photosynthesis limit the rate of photosynthesis in plants and organisms. Intermittent illumination of a culture by mixing provides a way to use a larger fraction of high-intensity sunlight falling on a given area. Essentially, the light-gathering mechanism (photosynthetic unit) can operate at a rate faster than can be accommodated by the dark reactions of photosynthesis.

Thus, the photosynthetic unit can use only a limited amount of light energy or quanta at a time. The phenomenon of light saturation is probably due to the internal mechanism whereby cells can photosynthesize with a very small amount of light. This saturation effect imposes a serious limitation on the efficiency of solar energy utilization by plants, algae, or photosynthetic bacteria.

For the case of a deep dense culture*, the incident light is fully absorbed. Mutual shading of the cells will then lead to two modes of light usage. Near the surface of the culture, cells exposed to $I > I_{sat}$ will be photosynthesizing in the saturation region and only a fraction of the available light will be used. All the light that penetrates to greater depths, where $I \leq I_{sat}$, will be used with maximum efficiency. The fraction, f, of photosynthetically active light that is used in photosynthesis is given by Equation A-1 (neglecting respiration).

$$f = \frac{I_s}{I_o} \left[1 + \ln \frac{I_o}{I_s} \right] \qquad (A-1)$$

---

*Arbitrarily defined to be ≥ 1 g dry cells/liter.

Using the saturation intensity of 1/10 of sunlight intensity (a common value) gives the fraction of light utilization as ~30%; the remaining 70% is wasted as heat.

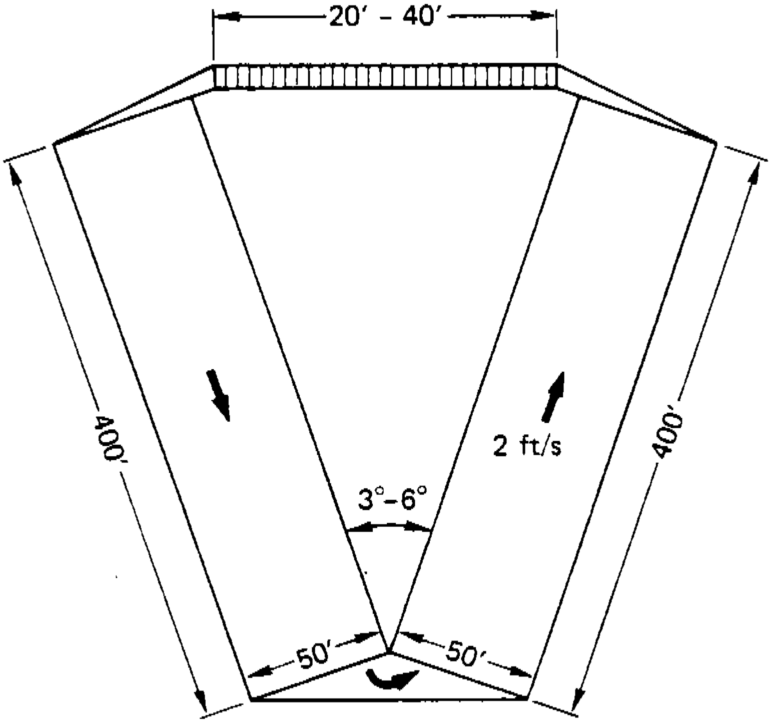
The problem then is to arrange the turbulent culture flow pattern so that the cells can use high-intensity sunlight as efficiently as weak light. The flow arrangement should be such that each cell will receive just its quota of light and then will immediately be replaced by another cell, so that none of the light will be wasted. What is required is a flow pattern of a very dense culture such that the cells will rapidly move in and out of a thin layer at the surface of the culture. Only while a cell is in this layer will it receive light. In this way the entire surface of the culture will always be occupied by cells that are utilizing all the incident light through the intermittent-light effect. The expected increase in yield can be found from equation A-1, being 1/f for a culture in which turbulent flow provides full light utilization. For full sunlight intensity the maximum increase in photosynthesis expected from mixing improvement alone could be as high as threefold ($1/0.33 \cong 3$). This increase in light use is expected before the intermittent light effect is fully realized. Exposing photosynthetic cultures to saturating flashes followed by dark periods equivalent to the dark reaction time constant of photosynthesis would then lead to an extra increase in light utilization efficiency. Thus, whereas equation A-1 predicts a threefold increase, a sixfold increase might be expected with the optimal intermittent light regime.

Potential Reactor Design

Wake interference flow and dense cultures have several advantages over the plug flow type of culture channel because optimum flash and dark intervals can be produced with regularity instead of the random pattern of intermittence found with highly turbulent flow. Only one-third the liquid head drop is required over a roughened channel to achieve the same eddy velocity near the surface as in a smooth channel (Davies, 1970). Good mixing of nutrients and dissolved gases is achieved in the flow patterns. The average light intensity with time can be maintained below the saturation intensity of the organisms, and photorespiration losses can be reduced. Variation of the recycle flow rate to adjust the culture cell mass concentration will provide a means of maintaining optimum conditions despite diurnal changes in light intensity.

If one could achieve a three- to sixfold increase in light utilization, it would be possible to maintain high cell concentrations. Such an increase in light use will be possible, however, only if energy input to the system is increased. Pumping represents the major energy input for the system. To maintain structured turbulence in the channels during an average of 8 hours of daily operation will require considerably more slope on the channels than that typically considered for a conventional plug flow design. (Pumping is done for only ~8 hours/day during the period of maximum light intensity.) For this analysis, a maximum of 2.0% slope has been calculated using the Manning equation and a coefficient "n" of 0.06. A one-acre channel surface area has been assumed as shown in Figure A-1.

The pumping energy requirements have been calculated for two channel slopes and flow depths in Table A-1. Two slopes were specified because no correlation now exists between flow conditions and the yield (using the intermittent light effect). It has been assumed that the pumps (Archimedes' screw pumps) will be driven by electric motors. Table A-2 summarizes the calculations concerning the amount of product hydrogen that would need to be burned to produce the electric power using an engine generator set.


20′ - 40′
400′
400′
2 ft/s
3°-6°
50′
50′

NOTE: Not to scale.

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FIGURE A-1 DIAGRAM OF CULTURE SYSTEM USED IN PRELIMINARY CALCULATIONS

Table A-1

CALCULATION OF ENERGY REQUIREMENTS FOR PUMPING

Basis: Channel depth of 5 cm
Channel length of 120 m
Channel width of 15 m

Channel Slope (%)	Pumping Station Lift, ft (m)	Pump* (HP)
1	10 (3)	31.5
2	20 (6)	63

85% motor efficiency

95% gear reducer efficiency

75% pump efficiency

$$\text{Motor HP} = \frac{(\ )\ \text{gpm} \times (\ )\ \text{lift} \times 8.33}{0.85 \times 0.95 \times 33000 \times 0.75}$$

Assume 0.6 m/s flow velocity throughout system

$$\text{Time exposed to light} = \frac{120\ \text{m}}{0.6\ \text{m/s}} = 200\ \text{s/channel} \cong 400\ \text{s total}$$

$$\text{Time exposed to dark} = \frac{15\ \text{m} + 15\ \text{m} + 6\ \text{m}}{0.6\ \text{m/s}} = 60\ \text{s}$$

$$\frac{\text{Time in light}}{\text{Total cycle time}} = \frac{400}{400 + 60} = 100 = 87\%$$

---

*For ~1 acre of channel surface.

Table A-2

CALCULATION OF FUEL REQUIREMENTS FOR PUMPING

Basis: Channel slopes of 1% and 2% (10- and 20-ft lifts)

Motor HP requirements of 31.5 and 63

275 Btu/SCF H_2

330 operating days per year

kWh/day = HP x 8 hr/day x 0.7457 kW/HP

Engine efficiency of ~ 27%

Generator efficiency ~ 92%

Total area = 1 acre

2×10^4 SCFD H_2/acre = 6.6 MM SCF/yr/acre

3414 Btu/kWh

% Scope	HP	kWh/Day	Btu/day*	SCF H_2/day	% of H_2 Produced per Channel
1	31.5	188	6.4×10^5	2.3×10^3	11.7
2	63	376	1.3×10^6	4.7×10^3	23.3

---

*Fuel requirement for engine/generator set operating on H_2. Engine/generator set has an overall thermal efficiency of 25%. Electric power is used to drive lift pumps.

Appendix B

OTHER GAS PURIFICATION SYSTEMS

This appendix describes various gas purification systems, including chemical absorption, physical absorption with water, cryogenic processes, palladium absorption and diffusion, and conversion of impurities.

Chemical Absorption Systems

The activated Benfield process is a modification of the hot potassium carbonate process by addition of an absorption catalyst and corrosion inhibitors. This process is primarily used for carbon dioxide removal from crude hydrogen and ammonia synthesis gas. The flow scheme (Figure B-1) of a Catacarb plant is identical to that used for the hot potassium carbonate process. When high-purity product gas is required, a split-stream cycle, with cooling of the stream flowing to the top of the absorber, and two- (or three-) stage regeneration are used. Carbon steel is a satisfactory material of construction for the entire plant.

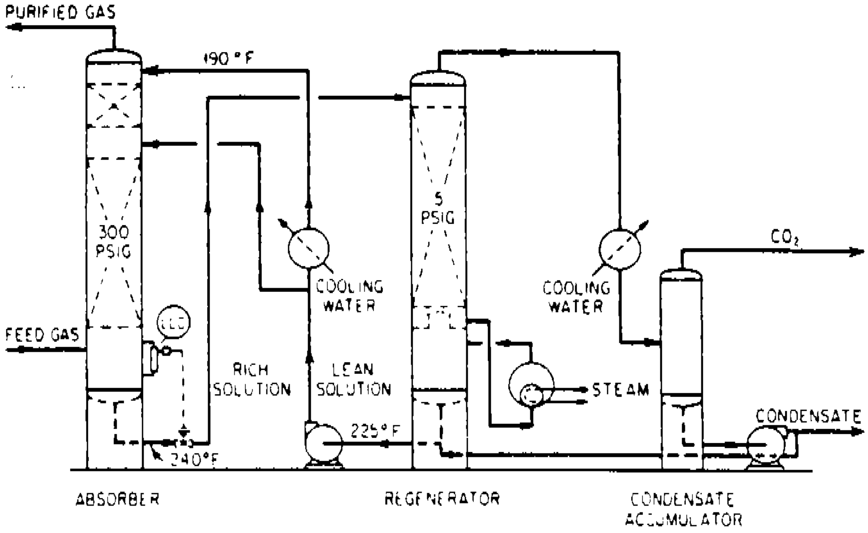
PURIFIED GAS
190 °F
5 PSIG
300 PSIG
CO$_2$
COOLING WATER
COOLING WATER
FEED GAS
RICH SOLUTION
LEAN SOLUTION
STEAM
CONDENSATE
225 °F
240 °F
ABSORBER
REGENERATOR
CONDENSATE ACCUMULATOR

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FIGURE B-1 FLOW DIAGRAM OF THE HOT POTASSIUM CARBONATE PROCESS FOR ABSORPTION OF CO$_2$

Physical Absorption with Water

The use of water for absorption of CO_2 is another option. The absorption of carbon dioxide in water has been shown to be almost entirely liquid-film controlled, presumably because of the relatively low solubility of carbon dioxide. In general, the process is limited to gas streams containing carbon dioxide at a partial pressure greater than 50 psi so as to ensure an economically useful CO_2 capacity of the water.

The volume of water required for acid gas scrubbing can be reduced if the equilibrium concentration of CO_2 can be increased. The equilibrium concentration of CO_2 in water at 18 atm (270 psia) is 0.8 g CO_2/100 g H_2O at 20°C. If a phosphate buffer is added to the water, a shift of the bicarbonate-carbonate system favoring a higher total carbon concentration in the water can occur.

The use of water as an absorbent offers the following advantages as compared to chemical absorbent solutions:

(1) Simple plant design (i.e., no heat exchangers or reboilers)
(2) No heat load
(3) Inexpensive solvent.

The principal disadvantages of the water process are

(1) Substantial loss of hydrogen (some can be recovered from intermediate pressure flash and recycled)
(2) Very high pumping load
(3) Poor CO_2-removal efficiency
(4) Impure by-product CO_2.

The high pumping load and poor CO_2 removal efficiency can be improved by increasing the CO_2 solubility in water with a buffer system. An intermediate pressure flash would lead to recovery of dissolved hydrogen and provide a relatively pure CO_2-water product.

The overall economics of the highly efficient chemical absorbent and physical absorbent and adsorbent systems has virtually eliminated water scrubbing processes from use. However, the water phosphate buffer scrubbing system may have an application. After the water solution is flashed to atmospheric pressure, it could be pumped into an aquatic biomass production process. One of the major shortcomings of large-scale aquatic biomass production is that of CO_2 supply. The phosphate-buffered water stream would provide a supersaturated stream (compared to pure water) of CO_2, a major growth-dependent nutrient (phosphate) and a buffered media for growth.

Cryogenic Purification

Low temperature cryogenic processes, such as liquid methane or liquid nitrogen scrubbing, are also capable of separating a wide range of impurity concentrations and yielding a high purity hydrogen. As is the case with absorption systems, these processes are generally preferable over adsorption and diffusion techniques for large-scale installations. Cryogenic and absorption procedures are generally selected on the basis of the combination of impurities to be removed and on the degree of separation desired.

Generally, cryogenic processing is preferable to absorption or diffusion methods where the feed rate is greater than 2-5 MM SCFD and the feed purity is lower than 90%. The nature of the cryogenic cycle will depend on the composition and condition of feed and product streams. High hydrogen purities can be realized by cooling to lower temperatures or by washing with liquid propane or methane (Numata, 1970; Streich, 1968). Cryogenic gas purification is well suited to cases such as N_2 and O_2, since these cases are relatively inert and are not as soluble in absorption solvents as CO_2. However, much lower temperatures ($-200^{\circ}C$) must be achieved to remove N_2 from H_2 than to remove CO_2 from H_2 ($-80^{\circ}C$) (see Figure B-2).

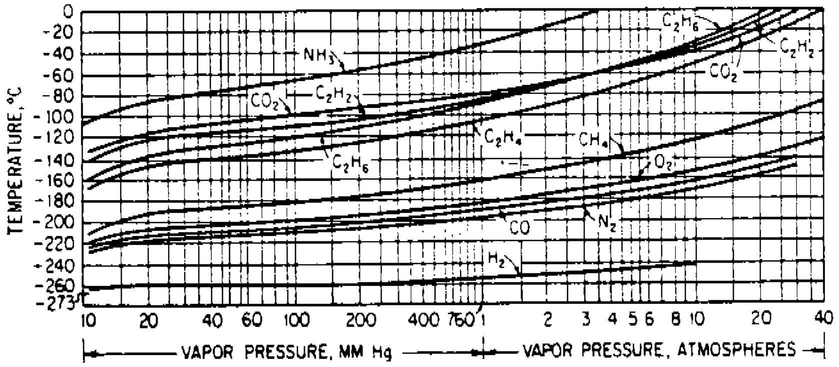

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FIGURE B-2 VAPOR PRESSURES OF VARIOUS GASES AT LOW TEMPERATURES (Stull, 1947)

Palladium Adsorption and Diffusion

Hydrogen at 315°C or higher readily diffuses through thin films (0.001 to 0.01 inch) of palladium metal or alloy that are completely impervious to all other gases. The rate of diffusion varies directly as the difference in hydrogen partial pressure on each side of the membrane and inversely as the membrane thickness. The diffusion rate has been expressed as the following equation by a number of investigators for the range from 0 to 760°C (Chiu, 1977; Makrides, 1966).

$$N_a = \frac{A}{t} (p)^{1/2} \exp(-B/RT)$$

where

N_a = hydrogen diffusion rate in cc STP/s/cm^2
A,B = constants related to the diffusion membrane
t = membrane thickness in cm
p = hydrogen partial pressure difference in atm
T = absolute temperature in °K
R = gas law constant.

Maximum hydrogen partial pressure difference is desirable for a given temperature and membrane thickness; thus, easily removable impurities, such as hydrocarbon and acid gases, are preferably separated beforehand. Then, a 99% hydrogen feed will yield a 99.99% hydrogen product.

Du Pont (1970) has developed hollow polyester fibers that are selectively permeable to hydrogen. A bundle of these fibers, which are about 36 μm OD and 18 μm ID, is contained in a pressure vessel about 18 feet long.

Hydrogen is concentrated as it diffuses from the pressure vessel into the fibers and then out the open end of the fibers. Capital investment for a commercial polyester fiber hydrogen diffusion unit is comparable to that of the equivalent capacity palladium installation, but the hydrogen product purity is lower (~97%).

The Prism separator by Monsanto can recover hydrogen from gas streams that contain more than 30% hydrogen with a pressure differential greater than 100 psi. This separation technique utilizes the relative permeation "speeds" to selectively separate a fast gas (e.g., hydrogen) from the components in the gas stream. However, these fiber diffusion systems are not applicable to this study since hydrogen, carbon dioxide, and water are all considered to be fast gases. Current applications of the prism separators are for the refining, petrochemical, and ammonia processing industries.

Conversion of Impurities

Impurities in hydrogen can often be converted to other impurities that are more easily removable or that are not prejudicial to the subsequent hydrogen usage. The conversion of carbon monoxide to carbon dioxide and hydrogen by the water gas shift reaction with steam is widely used for hydrogen gases where the carbon monoxide content is a few percent or less.

Carbon oxides can be hydrogenated to methane by a similar reaction but again, methanator units are typically used for hydrogen gases of high purity (>95%).

Appendix C

PRESSURE SWING ADSORPTION SYSTEM

PSA Adsorption Dynamics

In most adsorptive separation cases the process takes place in a dynamic system. The adsorbent is generally used in a fixed bed and the contaminated gas is passed through the adsorbent bed. Depending on the concentration and market value, the contaminant is either recovered or discarded when the loading of the adsorbent requires regeneration.

When a contaminant-containing fluid is passed through a bed of adsorbers, most of the adsorbate is initially adsorbed at the inlet part of the bed and the fluid passes on with little further adsorption taking place. Later, when the adsorber at the inlet end becomes saturated, adsorption takes place further along the bed. As more gas is passed through, the adsorption proceeds and the saturated zone moves forward until the breakthrough point is reached, at which time the exit concentration begins to rise rapidly toward the inlet concentration in the fluid. At this point the bed is near fully saturated. Whereas the concentration at saturation is a function of the material used and the temperature at which the unit is operated, the breakthrough capacity is dependent on the operating conditions, such as inlet concentration, fluid flow rate, and bed depth. The zone of the bed where the concentration gradient is present is often called the mass-transfer zone (MTZ). It is extremely important that the adsorber bed should be at least as long as the transfer zone length of the key component to be adsorbed.

The following factors play the most important role in length and rate of movement of the MTZ:

(1) The type of adsorbent
(2) The particle size of an adsorbent
(3) The depth of the adsorbent bed

(4) The gas velocity
(5) The temperature of the gas stream and the adsorbent
(6) The concentration of the contaminants to be removed
(7) The pressure of the system
(8) The removal efficiency required
(9) Possible decomposition of contaminants on the adsorbent.

Most industrial adsorbents are capable of adsorbing both organic and inorganic gases. However, their preferential adsorption characteristics and other physical properties make each one more or less specific for a particular application. Since adsorption takes place at the interphase boundary, the surface area of the adsorbent is an important factor in the adsorption process. Generally, the higher the surface area of an adsorbent, the higher its adsorption capacity for all compounds. However, the surface area has to be available in a particular pore size within the adsorbent. At low partial pressure (concentration) the surface area having the smallest pores into which the absorbate can enter is the most efficient. At higher pressures the larger pores become more important.

The action of molecular sieves* is slightly different from that of other adsorbents in that selectivity is determined more by the pore size limitations of the molecular sieve. It is important that the contaminant to be removed is smaller than the available pore size, and that the carrier gas is not adsorbed.

The dimensions and shapes of particles affect both the pressure drop through the adsorbent bed and the diffusion rate into the particles. The pressure drop is lowest when the adsorbent particles are spherical and uniform in size. However, the external mass transfer rate increases inversely with $d^{3/2}$ and the internal diffusion rate increases inversely as d^2. The pressure drop will vary with the Reynolds number, being roughly proportional to velocity and varying inversely with particle diameter. It is evident that adsorbent beds consisting of smaller particles, although causing a higher pressure drop, will be more efficient.

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*Molecular sieves are crystalline metal aluminosilicates with a three-dimensional interconnecting network structure of silica and alumina tetrahedra.

Theoretically there is no minimum or maximum velocity for the adsorption process to take place. The primary effect of gas velocity is on the rate of movement of the MTZ; however, gas velocity will affect the length of the MTZ if the rate-controlling step is changed when the superficial gas velocity is changed. A change from laminar to turbulent flow regime will change the rate-controlling step from bulk diffusion to pore diffusion. For many adsorbents the transition from laminar to turbulent flow takes place approximately at a modified Reynolds number of 10.

The physical adsorption capacity of any adsorbent will decrease with increasing temperature. At the same time, all diffusion rates will increase and the MTZ will be shorter while its rate of movement increases. The adsorption process is always exothermic. This increase in temperature of the bed ahead of the MTZ, during adiabatic operation of the adsorber, will decrease the equilibrium adsorption capacity of the adsorbent.

Increasing the adsorbate concentration of the influent gas into an adsorber will increase the rate of movement of the MTZ. All gases and vapors are adsorbed to some extent on all adsorbents. These gases, including carrier gases, compete for the available surface area and pore volume. Their effect will be to lower the adsorption capacity for the particular adsorbate to be removed. Water vapor, carbon dioxide, and any large-concentration, low-molecular-weight adsorbate will influence the adsorption capacity for the design adsorbate.

Although activated carbon is less sensitive to moisture interference than the more polar adsorbents (molecular sieve, silica gel, aluminas) at high moisture contents or high inlet relative humidities, its adsorption capacity will be considerably lower than that for adsorption from a dry gas stream.

Generally, the adsorption capacity of an adsorbent increases with increasing pressure, if the partial pressure of the contaminant increases.

If a carrier gas containing two or more adsorbates is introduced into an adsorbent bed, two or more MTZs form and travel along the adsorber at different rates. The absorbate least well adsorbed travels at the highest rate.

Regeneration

When an adsorbent bed reaches its capacity (breakthrough), the adsorbate can be removed from the adsorbent by several techniques. The most common ones are:

(1) Displacement of adsorbate
(2) Desorption of adsorbate
(3) Combustion of adsorbate.

On large adsorbers the typical regeneration practices are (1) and (2) or their combination. Combustion is generally practiced when the absorbate is very strongly adsorbed.

Several factors must be considered when establishing the conditions of regeneration for an adsorber system. It is important to establish if recovery of the contaminant is worthwhile, or only the regeneration of the adsorbent is required. The following factors must be considered when designing the stripping (desorbing) process:

(1) The length of time required for the regeneration should be as short as possible.
(2) The stripping direction should be opposite to the direction of the adsorption to permit the shortest route for the desorbed contaminant.

In the case of multicomponent adsorbate systems, one or more components may be completely removed from the adsorbent during regeneration, leaving only the more strongly adsorbed components.

System Design

Typical operational parameters for an adsorption bed are as follows:

	Range	Design
Superficial gas velocity	20–50 cm/s	40 cm/s
Adsorbent bed depth	3–10 MTZ	5 MTZ
Breakthrough time	0.5–8 hr	4 hr
Temperature	–200–50°C	--
Inlet acid gas concentration	100 ppm–40%	33%
Adsorbent particle size	0.5–10 mm	4–8 mm
Working charge	5–20% wt	10%
Adsorbent void volume	38–50%	45%
Regeneration time	1/2 adsorption time	

Appendix D

SPECIFICATIONS FOR GAS COMPRESSION

Stream composition (dry): 66.6% H_2, 33.3% CO_2

Inlet Temperature: 60°C ≡ 140°F

Inlet pressure: 15 psia

Outlet pressure: 260 psig

The properties of the gaseous mixtures in a hydrogen production facility are tabulated below.

Component	Mole%	Mole Wt.	Fractional MW	Molal Cp*†	Fractional Cp
H_2	66.6	2	1.3	6.93	4.62
CO_2	33.3	44	14.6	9.33	3.11
			Avg. MW = 16		Avg. Cp = 7.73

k ≡ the ratio of heat capacity at constant pressure, C_p, to that at constant volume, C_v. From thermodynamics $C_v = C_p - R$

$$k = \frac{C_p}{C_v} = \frac{C_p}{C_p - R} = \frac{7.73}{7.73 - 1.987} = 1.35$$

Assuming ideal gas behavior for three-stage compression, the compression ratio ≡

$$\left(\frac{P_2}{P_1}\right)^{1/S} = \left(\frac{260 + 15}{15}\right)^{1/3} = 2.64$$

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[*] Calculated from $Cp = \alpha + \beta T + \nu T^2$ data from Balzhiser et al (1972).

[†] 150°F assumed as an average temperature.

The discharge gas temperature is found by

$$T_2 = T_1 \left(\frac{P_2}{P_1}\right)^{\left(C_p - C_v \;/C_p\right)} = T_1\left(\frac{P_2}{P_1}\right)^{(k-1)/k}$$

$$T_2 = 600°R \left[2.64\right]^{(1.35 - 1)/1.35} = 772°R \equiv 312°F = 155°C$$

The work of compression per stage (neglecting pressure drop in heat exchangers) is found by

$$\text{Work} = \frac{k}{k-1} \cdot RT \left[\left(\frac{P_2}{P_1}\right)^{(k-1)/k} -1\right]$$

$$= \frac{1.35}{0.35} \cdot 1545 \frac{\text{lb ft}^3}{\text{ft}^2 \text{ lb mole °R}} \quad 600°R \left[(2.64)^{0.35/1.35} -1\right]$$

$$\cong 10^6 \frac{\text{ft lb}_f}{\text{lb mole stage}}$$

Assuming three stages, 1.9 MM SCFD, 391.6 $\frac{\text{ft}^3}{\text{lb mole}}$ and 5.05 x 10^{-7} $\frac{\text{hp hr}}{\text{ft lb}_f}$

Gives $10^6 \frac{\text{ft lb}_f}{\text{lb mole stage}}$ (3 stages) $\left[5.05 \times 10^{-7} \frac{\text{hp hr}}{\text{ft lb}}\right] \frac{1.9 \times 10^6 \text{ ft}^3/\text{day}}{391.6 \text{ ft}^3/\text{lb mole}}$

$$= 7500 \frac{\text{hp hr}}{\text{day}}$$

Compressor efficiency for a compression ratio of 2.5 is 80-89%. Assuming 85% compressor efficiency and a 95% motor efficiency, the total power requirement is then

$$\frac{7500}{0.95 \; 0.85} = 9300 \frac{\text{hp hr}}{\text{day}}$$

Deviations from ideal gas behavior can be significant at high pressures. For the above case a compressibility factor of 0.98 was found, revealing near ideal gas behavior. Thus no correction was made.

Appendix E

CO_2 ADSORPTION IN SOLUTION

(Letter Report to SERI)

January 19, 1981

Dr. Hilde Lindsey
Solar Research Institute
1536 Cole Boulevard (10/3)
Golden, Colorado 80401

Reference: Draft Report - (Technoeconomic Analysis of
A Hydrogen Production Process Using
Photosynthetic Bacteria
Contract No. BK-9-8281-02)

Dear Hilde:

You raised a good point during our recent discussion concerning the amount of CO_2 absorbed in solution. We did consider such absorption, and for the conditions we assumed, found such absorption to be unimportant. The calculations below will illustrate the point.

The absorption of CO_2 in solution will depend on the characteristics of the solution (initial CO_2 concentration, presence of buffers, initial solution pH) and the efficiency of mass transfer from gas bubbles to the solution. If we assume that mass transfer is not limiting, then CO_2 transfer will depend only on solution characteristics. For our base case, we assumed a concentration of a "CH_2O" substrate of 2.5 gm/ℓ and a gross H_2 production of 1 million scf/day or 28.3×10^6 liters/day. The volume of solution required to allow generation of this quantity of hydrogen was calculated to be 9.4×10^6 liters or roughly 5.3×10^8 gm moles of H_2O. The composition of the gas bubbles as generated will vary depending on the temperature because of the variation in the vapor pressure of water. At our assumed base case operating temperature of 60°C, the bubble composition will be as follows:

	Vol.%
CO_2	27
H_2	53
H_2O	20

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At a temperature of 35°C, which is the operating temperature level you now envision, the gas composition would be as follows:

	Vol.%
CO_2	31.9
H_2	62.6
H_2O	5.5

For high substrate concentrations, the solution will become saturated with CO_2, and after that point the gas bubbles as generated will be in equilibrium with the liquid phase. Under such a condition, the liquid phase CO_2 concentration can be estimated by the following method:

$$X_{CO_2} = \frac{P_{CO_2}}{H^\circ} \quad \left\{ \begin{array}{ll} X_{CO_2} & = \text{mole fraction of } CO_2 \text{ in solution} \\ P_{CO_2} & = \text{partial pressure of } CO_2 \text{ in atmospheres} \\ H^\circ & = \text{Henry's law coefficient} \end{array} \right.$$

$$\left. \begin{array}{l} H^\circ = 2.09 \times 10^3 \text{ at } 35°C \\ H^\circ = 3.41 \times 10^3 \text{ at } 60°C \end{array} \right\} \text{ Perry's Handbook, 4th edition, page 14-4}$$

$$\text{(at 35°C)} \quad X_{CO_2} = \frac{0.32 \text{ atm}}{2.09 \times 10^3 \text{ atm/mole } CO_2\text{/mole solution}} = \frac{0.15 \times 10^3 \text{ moles } CO_2}{\text{mole of solution}}$$

(or 370 mg/ℓ)

$$\text{(at 60°C)} \quad X_{CO_2} = \frac{0.27 \text{ atm}}{3.41 \times 10^3 \text{ atm/mole } CO_2\text{/mole solution}} = \frac{0.08 \times 10^{-3} \text{ moles } CO_2}{\text{mole of solution}}$$

(or 196 mg/ℓ)

Knowing the volume of the solution, and the equilibrium CO_2 concentration, one can estimate the total CO_2 absorbed as follows:

$$\text{(at 35°C)} \quad 5.3 \times 10^8 \text{ moles solu.} \times \frac{0.15 \times 10^{-3} \text{ mole } CO_2}{\text{mole of solution}} \simeq 79500 \text{ moles } CO_2$$

$$\text{(at 60°C)} \quad 5.3 \times 10^8 \text{ moles solu.} \times \frac{1.08 \times 10^{-3} \text{ mole } CO_2}{\text{mole of solution}} \simeq 42400 \text{ moles } CO_2$$

The total quantity of CO_2 generated per day is as follows:

$$28.3 \times 10^6 \text{ liters/d of } H_2 \times \frac{27 \text{ moles } CO_2}{53 \text{ moles } H_2} = 14.4 \times 10^6 \text{ ℓ } CO_2\text{/d}$$

$$\frac{14.4 \times 10^6 \text{ ℓ } CO_2\text{/d}}{22.4 \text{ ℓ/mole}} = 640{,}000 \text{ moles } CO_2\text{/d}$$

Therefore, at 35°C, about 12% of the CO_2 would be absorbed. AT 60°C, only about 7% would be absorbed. In either case, after equilibrium is reached, the composition of the gas requiring purification would be two moles of hydrogen to one mole of CO_2 on a dry gas basis.

The case we have selected for our base case analysis may be considered as a worst case in terms of CO_2 removal because the amount of CO_2 removed by absorption in the solution is negligible.

If one reduces the substrate concentration, the amount of gas generated per volume of waste decreases, and the fraction of the total CO_2 that is absorbed increases. For example, the CO_2 absorbed at a 1 gm/ℓ substrate concentration would be 33% of the total at 35°C and 16% at 60°C. The reactor costs would increase, however, on a per unit H_2 production basis.

After we have identified specific wastewater streams as possible substrates (as part of a separate SERI funded project) and SERI researchers have more fully defined the system in terms of operating temperature range, pH range, and cell mass concentration, I think it would be appropriate to prepare a more rigorous analysis that will include predictions of gas composition, the extent of CO_2 absorption, and the effect of CO_2 absorption on solution pH for specific wastestreams.

I suggest that this letter be incorporated as an appendix to the subject report to illustrate the fact that CO_2 absorption at high substrate concentrations is of little importance in terms of product gas purification requirements.

Very truly yours,

FOR JLJ

Jerry L. Jones, Director
Environmental & Biochemical Engrg.
Chemical Engineering Laboratory

JLJ/ak

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